The Toxic Substances Hydrology (Toxics) Program of the U.S. Geological Survey (USGS) provides earth-science information needed to prevent or mitigate contamination of the Nation's ground-water and surface-water resources. The Toxics Program's objective is to understand the movement and fate of toxic substances in the Nation's ground water and surface water. The program's research activities include (1) field and laboratory investigation of the physical, chemical, and biological processes that control the transport and fate of contaminants in ground water and surface water; (2) the development of new analytical methods and sampling techniques to measure the concentrations of toxic substances in water; and (3) the investigation of the relations among human activities, environmental characteristics, and regional patterns of water quality. Most of the research activities take place at contaminated sites. The major research objective is not characterization of contaminated sites, but is obtaining knowledge about contaminant-transport processes transferable to other contaminated sites. For example, the knowledge obtained at the research sites could be used to predict contaminant transport at other sites, improve methods for remediating contaminated ground water, design water-quality assessments, and identify potential causes of contamination.

Recent accomplishments of the Toxics Program have been presented at a series of technical meetings held in Tucson, Arizona (1984), Cape Cod, Massachusetts (1985), Denver, Colorado (1987), Pensacola, Florida (1987), Phoenix, Arizona (1988), and Monterey, California (1991). This report documents the oral and poster presentations given at the most recent meeting, held in Colorado Springs, Colorado, in September 1993. The sections in this report correspond to the topical organization of the meeting's oral sessions. Each session focused on research at a specific contaminated site or on a topical subject. Papers associated with poster sessions were integrated into the appropriate section. The lead paper in most of the sections gives an overview of the research conducted at the site discussed.

Section A addresses the biodegradation of gasoline in ground water that resulted from a leaking underground storage tank in Galloway Township, New Jersey. The papers describe methods to determine in situ biodegradation rates of gasoline on the water table, the geochemistry of gasoline constituents dissolved in ground water, and air-flow modeling of gas transport in the unsaturated zone.

Section B describes fluid flow and solute transport in fractured rock at the Mirror Lake Site in New Hampshire, where methods to characterize contaminated fractured rock are being developed. The methods are interdisciplinary and draw on techniques from hydrology, geology, geochemistry, and geophysics. Specific examples of papers are (1) discussions on the use of well logs to help design tracer tests and (2) comparisons of subsurface fracture mapping with electromagnetic and seismic tomography and with borehole acoustic televiwer and borehole flowmeter logs.

Section C contains papers on the migration of sewage-contaminated ground water on Cape Cod, Massachusetts, and on the transport and fate of metals, microbes, and organic chemicals in ground water. The papers describe the use of a large array of multilevel samplers to conduct large- and small-scale (hundreds of meters to meters) tracer tests designed to study a variety of transport processes in ground water. Examples of topics of additional papers in this section include: phosphate contamination in ground water, the role of protozoa in an organically contaminated aquifer, and numerical simulation of contaminant transport.

Section D is on the biodegradation and transport of chlorinated solvents, such as trichloroethylene (TCE), in ground water at Picatinny Arsenal, New Jersey. The papers describe the desorption of TCE from aquifer sediments, the microbial degradation and transport of TCE in ground water, the volatilization and transport of TCE in the unsaturated zone, and the surfactant-enhanced remediation of ground water contaminated with TCE.

Section E presents the development of methods to analyze and collect water samples, and to investigate transport processes. These papers discuss, for example, the development of a new method to collect sediment cores without loss of sample, new analytical methods to measure the concentrations of pesticides and pesticide metabolites in water, and the use of nitrogen isotopes to study the subsurface transport of nitrogen.

Section F contains papers on the environmental fate of agricultural chemicals in the Midwest. The papers describe the occurrence, distribution, and transport of agricultural chemicals in ground water, streams, large rivers, reservoirs, and precipitation at
regional to test plot scales. Examples of specific topics in this section are papers on the relation of nitrate concentrations in surface water to land use, the persistence of herbicides in reservoirs, and the results of a reconnaissance of pesticides in near-surface aquifers. The final eight papers in this section present results from the Management Systems Evaluation Areas (MSEA) program, which is part of an interagency research program to evaluate the effects of agricultural-management (farming) systems on water quality.

Section G contains papers on the natural biodegradation and transport of crude oil in the subsurface at Bemidji, Minnesota. The papers describe crude-oil contamination that resulted from a pipeline failure. Because the time the contamination occurred and the amount of crude oil in the subsurface are known, this site has provided USGS researchers and others a unique opportunity to study contaminant hydrology; information on the source of contamination usually is not available for most sites of groundwater contamination. Examples of specific topics in this section are papers on the use of simulation to study field-scale solute transport and biodegradation, and on small-scale chemical heterogeneities in the contaminated aquifer.

Section H focuses on the fate of anthropogenic contaminants in the San Francisco Bay Estuary and tributaries in California. The papers describe the transport of pesticides from the San Joaquin and Sacramento Rivers, California, through the Sacramento-San Joaquin Delta, and into the Bay. In addition, the papers in this section describe the fate of organochlorine compounds, the results of a survey of molecular marker compounds, and the distribution and flux of sulfides in the Bay.

Section I contains papers on the transport and fate of toxic metals in acidic mine drainage in the headwaters of the Upper Arkansas River in Colorado. Results of tracer and pH-modification experiments in St. Kevin Gulch, Leadville, Colorado—a small mountain watershed—are discussed. These experiments were designed to isolate hydraulic transport processes so that geochemical processes can be studied.

Section J addresses a variety of topics relating to the hydrology of toxic substances in ground water and surface water. The papers are grouped by topic, and discuss, for example, the fate of organic compounds in surface water, the fate of hydrocarbons in the subsurface, the microbial degradation of explosive wastes, and the measurement of unsaturated-zone properties.

Section K reports on the transport of agricultural chemicals in ground water at an agricultural research plot near Plains, Georgia, where USGS and U.S. Department of Agriculture researchers collaborated on a tracer test involving bromide, atrazine, and other agricultural chemicals beneath a plot of irrigated corn. The papers discuss, for example, the two-dimensional distribution of a bromide tracer in the unsaturated zone, and the spatial variability of soil properties affecting the transport of agricultural chemicals.

Section L contains papers on nonpoint sources of groundwater contamination. These papers, which report results of studies on Long Island, New York, and the New Jersey coastal plain, describe the relation between land use and groundwater contamination.

Section M presents papers on acidic groundwater and surface-water contamination from copper mining near Pinal Creek, Arizona. The papers discuss, for example, the use of groundwater age dating to confirm estimates of travel times, the interaction of the contaminant plume with Pinal Creek, and the relations among algal species and chemical gradients in Pinal Creek.

Compiling and editing a proceedings of this size is a complex and difficult task. The task was made easier by the work and dedication of David Aronson, who died on April 7, 1996. David coedited two proceedings of technical meetings for the Toxic Substances Hydrology Program, and received awards for his work. This proceedings is a testament to his many contributions to the U.S. Geological Survey.

David W. Morganwalp
Acting Coordinator
Toxic Substances Hydrology Program
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Overview of Research on the Transport, Microbial Degradation, and Remediation of Hydrocarbons at a Subsurface Gasoline-Spill Site in Galloway Township, New Jersey

By Arthur L. Baehr and Jeffrey M. Fischer

Abstract

Since 1988, the U.S. Geological Survey has conducted research on the fate and transport of hydrocarbons at a site of subsurface gasoline contamination in Galloway Township, New Jersey. Work has focused on three interrelated areas of research: ground-water contaminant geochemistry, estimation of microbial degradation rates of hydrocarbons on the basis of rates of gas transport in the unsaturated zone, and vapor-extraction remediation design. Contaminant-geochemistry work has produced a water-quality data base that indicates zones of aerobic degradation adjacent to zones of anaerobic degradation with sharp chemical-concentration gradients in narrow interfacial zones. The analysis of gas transport in the unsaturated zone has provided a method for quantifying rates of aerobic hydrocarbon biodegradation in the capillary zone and shallow ground water. Mathematical models have been developed to simulate vapor-extraction remediation and to optimize system design. Research activity in each area is detailed and the project bibliography is updated.

INTRODUCTION

In 1988, the U.S. Geological Survey (USGS) began a field-oriented research project at a site of subsurface gasoline contamination from a leaky underground storage tank on a farm in Galloway Township, New Jersey (fig. 1). The objective of the original project, which was conducted in cooperation with the New Jersey Department of Environmental Protection and Energy, was to determine factors controlling the performance of vapor-extraction remediation. During the installation and sampling of the initial monitoring network in the fall of 1988, it became clear that the site afforded a unique opportunity to conduct field and laboratory research on the fate and transport of hydrocarbons in the subsurface.

The scope of the project was expanded to allow for more extensive characterization of contamination in the unsaturated zone and shallow ground water before site remediation. The project data base provides for evaluation of the natural attenuation and microbial degradation of hydrocarbons. In 1989, the site was selected as a USGS Toxic Substances Hydrology program research project. The project work plan in its formative stage was presented at the technical meeting held in Monterey, Calif., in 1991. The purpose of this paper is to summarize research activity and update the project bibliography to include results reported since the Monterey meeting.

The Galloway Township study site is located in the New Jersey Coastal Plain about 30 mi northwest of Atlantic City (fig. 1). Unconsolidated sediments beneath the site are mostly medium-grained sands, with some clay layers. The unsaturated zone is typically about 9 ft thick. Its lower boundary is a perched water table which, depending on precipitation history, may be coincident with the regional water table.

Ground water in the regional aquifer usually flows to the southeast. Fischer, Smith, and Baehr (1996) describe the hydrogeology of the site. The monitoring network (fig. 1) consists of 27 nests of vapor probes, 13 ground-water monitoring wells, 2 multilevel ground-water samplers, 5 vapor-extraction wells, 2 neutron-probe access pipes, and a nest of thermistors (Fischer and others, 1991). The composition of unsaturated-zone gases is determined by analysis of gas samples collected from the vapor-probe network (Baker and others, 1991). Ground-water contamination and inorganic chemistry is determined by analyzing samples collected from wells and submerged vapor probes (Baedecker and others, 1991; Cozzarelli and others, 1991). Gibbs and others (1993) report on the construction and sampling of the multilevel samplers.

1U.S. Geological Survey, West Trenton, N.J.
Figure 1. Location of subsurface gasoline-spill study site in Galloway Township, N.J.
Results of initial studies at the site revealed that gasoline was present as a separate-phase liquid on the regional water table in the immediate vicinity of well DEP-1 and on the perched water table in the vicinity of the exhumed tank (fig. 1). Dissolved hydrocarbons identified include benzene, toluene, C_2-C_3, C_4-alkyl-benzenes, and naphthalene (Baedecker and others, 1991; Phinney and Cozzarelli, 1996). The areawide distribution of contaminants was described by Baedecker and others (1991) and Fischer, Smith, and Baehr (1996). Contamination in perched water has persisted at high concentrations in the vicinity of the exhumed tank. Hydrocarbon contamination on the regional water table is downgradient from the source and concentrations vary with time, depending on the direction of groundwater flow. The concentration of total aromatic hydrocarbons decreases downgradient, as a result of dilution, volatilization, and biodegradation.

Ground water was sampled and analyzed to identify biogeochemical processes occurring at the site and to identify degradation pathways. Baedecker and others (1991) and Cozzarelli and others (1991), provide descriptions of the sampling methods. Results of analyses for inorganic and organic chemical compounds indicate active microbial degradation of hydrocarbons in ground water. These data are reported by Baedecker and others (1991), Cozzarelli and others (1991), Cozzarelli (1993), and Cozzarelli and Baedecker (1996).

Aerobic respiration and reduction of nitrate, sulfate, and iron oxides by microbes have been identified as important processes for degrading hydrocarbons at the site (Baedecker and others, 1991; Cozzarelli and others, 1991). The perched water has been depleted of dissolved oxygen and nitrate, leaving sulfate and iron reduction as the main biodegradation processes. In the regional aquifer, aerobic respiration and nitrate reduction appear to be the main hydrocarbon-degradation pathways as evidenced by results of multilevel sampling beneath the water table. Results of microbial counting showed higher numbers of hydrocarbon-degrading microorganisms in contaminated ground water and sediment than in uncontaminated ground water and sediment (Mills and Randall, 1991). The fate of organic acids, which are intermediate hydrocarbon-degradation products, depends on the availability of electron acceptors for anaerobic degradation processes (Cozzarelli, 1993).

Environmental regulators concerned with the effect of gasoline spills on ground-water quality have recently acknowledged that microbial degradation of hydrocarbons is a significant mechanism for attenuating subsurface gasoline contamination. Methods for quantifying degradation rates at a given site, however, have not been established. The approach developed for the Galloway Township site is to identify stoichiometric relations among oxygen consumption, carbon dioxide production, and hydrocarbon degradation. Once these relations are established, fluxes of oxygen and carbon dioxide through the unsaturated zone are used to estimate in situ biodegradation rates.

Baehr and others (1991) provide an overview of this method. Oxygen diffuses toward the water table where it is used by microbes to aerobically degrade hydrocarbons. Carbon dioxide, which is an end product of this degradation, diffuses toward the surface. At the Galloway Township site, hydrocarbons are not detected in the gaseous phase in most parts of the unsaturated zone, whereas the underlying perched water is virtually anoxic and contains high concentrations of dissolved hydrocarbons (Cozzarelli and others, 1991; Cozzarelli, 1993). These data, combined with the presence of an abundance of hydrocarbon-degrading bacteria at the water table (Mills and Randall, 1991), indicate that aerobic hydrocarbon degradation occurs near the top of the perched water. Thus, the rates of oxygen and carbon dioxide transport are related to the rate of aerobic degradation of hydrocarbons.

The relation between the rates of oxygen consumption and carbon dioxide production by hydrocarbon-degrading bacteria is complicated by the oxidation of ferrous iron. Also, the presence of intermediate metabolites, such as organic acids, detected in the ground water (Cozzarelli, 1993) indicates that aerobic degradation is not always complete. If these pathways can be neglected for the purpose of determining an approximate stoichiometry, then complete hydrocarbon mineralization (for example, for toluene: C_7H_8 + 9O_2 → 7CO_2 + 6H_2O) may provide a working approximation.
This working approximation was substantiated in the laboratory by conducting respiration experiments with hydrocarbon-contaminated sediment (Noland, 1993; Noland and others, 1996). Furthermore, Lahvis (1993) determined that the ratio of oxygen and carbon dioxide fluxes in the unsaturated zone above contaminated perched water at the Galloway Township site was close to that predicted by using the mineralization working approximation.

A value for the effective diffusion coefficient for a constituent in unsaturated porous media is required for calculating diffusion rates through the unsaturated zone. Cores of sediment were extracted from the unsaturated zone at the Galloway Township site and a technique was developed for estimating effective diffusion coefficients (Fischer, Baker, and Baehr, 1996). The method involves measuring changes in tracer concentration along the length of the core. A mathematical model developed by Baehr and Bruell (1990) is used to calculate the effective diffusion coefficient.

Two types of field experiments were conducted to evaluate hydrocarbon-biodegradation rates. The first experiment involves measuring oxygen and carbon dioxide profiles at the site under natural conditions prior to remediation. The second experiment involves monitoring the redistribution of gases after a period of vapor extraction has caused oxygen concentrations to increase and carbon dioxide concentrations to decrease in the unsaturated zone to near-atmospheric levels. A vapor-transport model developed by Lahvis (1993) is used to compute rates of gas movement from gas-phase concentration data. Lahvis and others (1996) conclude that the rates of gas movement at the Galloway Township site indicate that significant rates of hydrocarbon degradation may be limiting the spread of the contaminant plume in ground water.

Water-quality data collected by sampling near the perched water table indicate that the aerobic degradation rate is highest in a small vertical interval between the top of the capillary zone and 1 ft below the water table. This information leads to the formulation of the hypothesis that coexisting conditions of high moisture content and high concentrations of oxygen and hydrocarbons, which prevail only within this small vertical interval, are more favorable for the aerobic degradation of hydrocarbons than those in the relatively dry overlying unsaturated zone and underlying anoxic ground water. Construction of a field experiment to study these conditions over the indicated spatial scale was not possible as a result of perched water-table altitude variations. Therefore, a laboratory method to emulate biochemical conditions near the water table was developed (Baker, 1993). Sediment collected just above the water table was packed in glass columns. The upper part of the column was unsaturated and the column water level was maintained at a constant altitude. Hydrocarbon concentration was maintained as a constant level in the saturated lower part of the column. Concentrations of hydrocarbons, oxygen, and other constituents can be controlled by manipulating the end reservoirs. Analysis of these experiments with a one-dimensional vapor-transport model is reported by Baker (1993) and Baker and Baehr (1996). Hydrocarbon-degradation rates within sediments maintained near capillary-zone moisture conditions were an order of magnitude higher than those in the drier overlying unsaturated sediments. Neither hydrocarbon concentrations nor oxygen concentrations were limiting factors in these experiments.

**VAPOR-EXTRACTION-REMEDIATION DESIGN**

Remedial action for spills of petroleum products generally include an effort to physically recover product accumulated on the water table by pumping or bailing. Substantial portions of the spill typically remain trapped in residual saturations in the unsaturated and capillary zones as well as in a smear zone in shallow ground water caused by fluctuating water-table altitudes. This part of the spill can pose a long-term threat to ground-water quality, because it is a source of hydrocarbons that can be transported in aqueous and gaseous phases. Vapor-extraction technology has been applied successfully to remove additional hydrocarbons from the residual saturation source. The success of this technology is based on the significant volatility of gasoline hydrocarbons and the ability to induce an air-flow field in the unsaturated zone with combinations of dry wells and trenches.

Mathematical models of the air-flow field can be used to help design a vapor-extraction system. The ground-water-flow simulator MODFLOW (McDonald and Harbaugh, 1988) has been adapted for this purpose. This code, called AIR3D, and a users' manual currently are in preparation for distribution in the public domain. Application of the air-flow code results in the definition of the air-flow field corresponding to a chosen configuration of extraction and injection locations. Welty and others (1992; 1996) extended the modeling tool by coupling the three-dimensional air-flow model with mathematical programming to define an optimal configuration of extraction and injection locations. Publication of the computer code that implements this coupling, called OPTAIR, and a users' guide in the public domain is planned.
The permeability of unsaturated porous media to air is required information for air-flow simulations. Baehr and Hult (1991) developed analytical solutions to the equation defining air flow to or from a single well screened in an unsaturated zone to determine air-phase permeability from results of pneumatic tests conducted at a research site near Bemidji, Minn. A computer code that implements the analytical solutions has been developed. The code, called AIR2D, and a users’ manual is currently in preparation for publication in the public domain. Joss and others (1992) report on applications of this parameter-estimation technique at the Galloway Township site.

A mathematical model for simulating chemical transport associated with vapor extraction and bioventing has been developed by Joss (1993). The model can be used to simulate three-dimensional, coupled transport of multiple chemical species and is expected to be a useful tool in analyzing and designing vapor-extraction, bioventing, and air-sparging remediation systems. This model is summarized by Joss and Baehr (1996).

REFERENCES


Hydrogeology, Contaminant Distribution, and Biodegradation Processes at a Gasoline-Spill Research Site in Galloway Township, New Jersey

By Jeffrey M. Fischer¹, Nicholas P. Smith¹, and Arthur L. Baehr¹

Abstract

The hydrogeology of the Toxic Substances Hydrology Program research site in Galloway Township, New Jersey, was characterized to determine factors controlling hydrocarbon-contaminant distribution and biodegradation. Sediments beneath the site are predominantly sand and clay. A localized zone of perched water forms above the regional water table. The direction of regional ground-water flow in the unconfined aquifer has varied from slightly north of east to east-southeast. Horizontal hydraulic gradients have been less than 0.005 since 1988 and estimates of average horizontal linear velocities range from 0.04 to 0.36 feet per day. A monitoring well provides a conduit for water to flow down from the perched water table zone to the unconfined part of the regional aquifer. The direction of ground-water flow near this well differs from regional flow directions.

Gasoline as a separate-phase liquid is floating on the regional water table in the leaky monitoring well and in the perched water zone near the location from which the tank was exhumed. Dissolved hydrocarbons are present in the perched-water zone within a stable elliptical plume about 80 feet long and 40 feet wide in the 11 to 14 foot depth interval. Hydrocarbon contamination in the unconfined aquifer was detected downgradient from the leaky well, but contaminant location varied with changes in the direction of ground-water flow. The concentration of total aromatic hydrocarbons decreased downgradient as a result of dilution, dispersion, and biodegradation. Ground-water flow affects the types of hydrocarbon-degradation processes and, thus, the locations in which hydrocarbon contaminants are found.

INTRODUCTION

Contamination of ground water with gasoline hydrocarbons is a serious problem throughout the United States. In the subsurface the constituents of gasoline move as solutes, as vapors, or as an immiscible phase, and can undergo microbial degradation. An understanding of the processes that control the transport and biodegradation of gasoline is needed to provide a strong scientific basis for evaluating the threat to ground-water supplies from gasoline spills.

In 1984, gasoline was found to have leaked from an underground storage tank at a farm in Galloway Township, New Jersey (fig. 1). Investigations by State agencies revealed a localized area of shallow ground water contaminated with gasoline hydrocarbons. No contamination was detected in offsite shallow domestic wells or in onsite deep irrigation wells. The leaking tank was removed in May 1986, and contaminated soils were excavated to a depth of 8 ft from an area about 80 ft long and 25 ft wide (fig. 1). The excavation was backfilled with uncontaminated sediments.

In 1988, the U.S. Geological Survey (USGS) began investigations at the site. Objectives of these investigations are described by Fischer and others (1991) and Baehr and Fischer (1996). This paper describes the hydrogeology and geochemistry of the research site, and discusses the relations among the hydrogeology, contaminant distribution, and biodegradation processes at the site.

Since the Galloway Township farm was chosen as a USGS research site in July 1988, an extensive network of multilevel probes and wells has been installed for observing small-scale vertical chemical gradients immediately above and below the water table. The ground-water-monitoring network (fig. 1) consists of 13 monitoring wells, 2 multilevel ground-water samplers, 27 nets of submerged vapor probes, and 5 vapor-extraction wells. To identify dissolved hydrocarbons and inorganic constituents that are
Figure 1. Location of Galloway Township research site showing former tank location, area of excavation, and ephemeral drainage channel. (Section A-A' shown in fig. 2.)
indicators of hydrocarbon biodegradation, ground-water samples were collected in June 1989, January 1990, July 1990, and April 1991. The monitoring network is described in detail by Fischer and others (1991). Ground-water sampling and analytical procedures, as well as a detailed discussion of the ground-water chemistry, can be found in Baedecker and others (1991) and Cozzarelli and others (1991).

**HYDROGEOLOGY**

The research site is located in a sparsely populate agricultural section of Galloway Township, in Atlantic County, New Jersey. The area is relatively flat and no perennial streams or surface impoundments are present within 0.25 mi of the site. During periods of heavy rain, runoff is channeled across the site in an ephemeral drainage channel (fig. 1). Measured precipitation at the research site was 40, 45, and 39 in. in 1990, 1991, 1992, respectively.

The site is situated in the Coastal Plain physiographic province and is underlain by seaward-dipping wedges of unconsolidated sediments composed of sand, silt, and clay. Near-surface sediments consist of fluvial sands and clays. The sands are predominantly quartz with minor microcline and ilmenite. Clays near the surface are mostly gibbsite, whereas deeper clays are kaolinitic (Owens and Minard, 1979). Core samples and geologic logs obtained during installation of the vapor probes and wells were used to describe the lithology within 25 ft of the land surface (fig. 2). Records of domestic and irrigation wells at the site and on adjacent properties were used to examine the lithology at greater depths and to assess the areal extent of the lithologic units.

![Figure 2](image-url)
The research site overlies the Cohansey aquifer. The ground-water-flow system beneath the site consists of two hydrologic units that were studied in detail: a zone of perched water of local extent and an unconfined aquifer of regional extent (hereafter referred to as the "regional aquifer"). The perched-water zone forms above the dense clay stringers that are present at depths of 14 to 19 ft (fig. 2). Measurements of moisture contents less than saturation beneath the clay stringers and the ability to draw vapors from probes situated between the base of the clay stringers and the top of the regional aquifer confirm that the clays are responsible for the presence of the perched water. Records of offsite wells indicate that the upper part of the regional aquifer is separated from the lower part by an areally extensive, 20-ft-thick clay layer, the upper surface of which is at a depth of about 40 ft. Because initial study results from the site indicated that no hydrocarbon contaminants were present in the lower part of the regional aquifer, USGS studies were limited to the perched-water zone and the upper part of the regional aquifer.

The depth of the regional water table has varied from 13.8 to 20.9 ft below land surface since water-level measurements were first made at the site in March 1988. The horizontal hydraulic gradients has usually been less than 0.005. Directions of ground-water flow vary in response to precipitation and irrigation withdrawals. Since May 1989, the usual ground-water flow direction has been to the east, and normally has ranged from slightly north of east to east-southeast (fig. 3). Occasionally, flow has been to the east-northeast or southeast. Results of slug tests conducted at monitoring wells in the regional aquifer, and analyzed according to the method of Hvorslev (1951), indicate that horizontal hydraulic conductivities range from about 2 to 30 ft/d. Hydraulic conductivities at two adjacent wells, DEP-1 and EVW8D, were lower than those measured at other wells (about 0.2 ft/d). Well records indicate that these two wells may be screened in a clayey part of the regional aquifer. On the basis of hydraulic-conductivity measurements, hydraulic-gradient data, and an average porosity of 0.41, the average linear flow velocity in the regional aquifer was estimated to range from about 0.04 to 0.36 ft/d.

The depth of the perched water table varied from 8.0 to 12.4 ft below land surface from May 1990 to December 1992. The perched water table is highest near the ephemeral drainage channel (fig. 1). Because runoff infiltrates along this channel, the perched water table slopes away from the channel and ground water flows perpendicularly away from it (to the northwest and southeast; fig. 2). Slug tests conducted in the perched-water zone indicate the horizontal conductivities of the sands that are present at depths of 4 to 11 ft range from 8 to 30 ft/d. Deeper interbedded sands and clays, at a depth of 11 to 14 ft, are presumed to have lower horizontal hydraulic conductivities. The perched-water zone varies in areal extent and thickness with precipitation, but it usually is present within a 70-ft radius of the location of the exhumed gas tank. During dry periods, the southeastern part of the perched-water zone, in the vicinity of well USGS-5 (fig. 1), disappears entirely. Several factors may account for this observation. The slope of the clay stringers may cause ground water to flow toward the northwest during dry periods (fig. 2); sand units with relatively high hydraulic conductivity may grade into clayey sands of lower hydraulic conductivity; or the characteristics of the clay stringers, such as their thickness or hydraulic conductivity, may vary and cause changes in percolation rates.

Perched water eventually leaks down to the regional aquifer; however, the degree of connection between the perched-water zone and the regional aquifer is uncertain. On a seasonal basis the regional water table rises and completely saturates the zone beneath the clay stringers. Baedecker and others (1991) concluded, on the basis of chemical gradients, that the clay stringers hinder mixing between the perched-water zone and the regional aquifer. Measured hydraulic conductivities of cores indicate that the clays are relatively impermeable (10-5 to 10-7 ft/d). During the study period, water levels in the perched-water zone were 5.3 to 9.6 higher than those measured in the regional aquifer. This difference produced very high vertical gradients; however, the low permeability of the clay stringers limits contact between the two water zones. Estimated vertical fluxes through the clay stringers were less than 1 in/yr and flow velocities were less than 2 in/yr.

The annular space around well DEP-1, a monitoring well installed prior to USGS investigations, appears to provide a conduit for the downward flow of water and gasoline from the perched-water zone to the regional aquifer. Evidence for this connection includes the following: The record of well DEP-1 indicates that the top of the screen is in the clay stringers and that the sand pack extends up into the perched-water zone; water-level altitudes in well DEP-1 are consistently...
EXPLANATION

--- 41.2 --- Water-level contour—Shows altitude of water level in feet. Dashed where approximate. Contour interval is variable. Datum is sea level

- Location of monitoring well used for water-table-altitude measurement

Figure 3. Water-level altitudes at the Galloway Township research site in January 1990, July 1990, and April 1991. (Water levels in well DEP-1 were approximately 0.75, 0.70, and 1.10 feet higher than regional water levels in January 1990, July 1990, and April 1991, respectively.)
higher (from 0.3 to 1.5 ft, depending on time of year) than those in nearby wells (fig. 3), and water-level data from vapor probe borings indicate that the perched water table is depressed in the vicinity of well DEP-1. Elevated regional water levels near this well indicate that local directions of ground-water flow are radially away from the well and vary significantly from regional flow directions (fig. 3). In addition, ground-water flow rates must be greater in the vicinity of this well than elsewhere in the regional aquifer, and vertical flow must be significant. The amount of leakage varies over time as vertical gradients changes.

**CONTAMINANT DISTRIBUTION AND DEGRADATION PROCESSES**

From the beginning of the field study in September 1989 until December 1991, gasoline as a separate-phase liquid was detected only on the regional water table in well DEP-1 (fig. 1). From September 1989 to March 1990, the thickness of gasoline in the well decreased from about 1.2 ft to less than 0.05 ft. From April 1990 through January 1991, only a slight sheen of gasoline was detectable in the well; minor amounts (less than 0.03 ft) reappeared in the well from February 1991 through October 1991. No separate-phase gasoline has been detected in well DEP-1 since January 1992.

Vapor sampling, begun in July 1989, indicated the presence of separate-phase gasoline on the perched water table in the area where the tank had been (fig. 1). Much of the separate-phase gasoline has been removed from the perched-water zone as a result of vapor-extraction experiments begun in October 1990. (See Baehr and Fischer (1996) for a description of vapor-extraction experiments at the site.) Hydrocarbon vapors have not been detected above the perched-water zone since August 1992; it is presumed that very little separate-phase gasoline has been present since then.

Aqueous-phase-hydrocarbon contamination in the perched-water zone consists of a small elliptical area about 80 ft long by 40 ft wide at a depth of 11 to 14 ft (fig. 4). Studies by Baedecker and others (1991) indicate that the total concentration of benzene, toluene, ethylbenzene, o-xylene, m-xylene, and p-xylene (BTEX) within this area usually exceeded 2 mg/L. Hydrocarbon concentrations in the center of this plume have remained fairly stable over time, possible as a result of low rates of ground-water flow in the interbedded sand and clay layers at the base of the perched-water zone. Hydrocarbon concentrations decrease toward the sides and top of the plume, partly as a result of dilution. Hydrocarbon concentrations in the southeastern limb of the plume have decreased considerably over time (fig. 4).

In the regional aquifer, concentrations of aqueous-phase hydrocarbons and their areal distribution have varied substantially during the study period as a result of changes in ground-water flow directions. Generally, hydrocarbon contaminants were detected downgradient from areas where ground water leaks through the clay stringers. These areas usually were downgradient from well DEP-1. Thus the areal distribution of BTEX was east of well DEP-1 in January 1990, southeast of the well in July 1990, and east of the well in April 1991 (fig. 5). In July 1990, the plume was narrow, possibly because the direction of ground-water flow was relatively constant for the 4 months prior to sampling. The plume was much broader in July 1990 than it was during the other two sampling periods possibly because the direction of ground-water flow was highly variable during the 4 months prior to sampling. The plume location is consistent with flow directions if solute-transport times are considered. Total BTEX concentrations in the center of the plume in the regional aquifer often exceed 10 mg/L (fig. 5). The concentration of total aromatic hydrocarbons decreases downgradient, in part as a result of dilution and dispersion. Compositional changes from lighter weight to heavier weight aromatics are indicators of volatilization and biodegradation along the flow path. The contaminant plume flows 5 to 10 ft beneath the top of the regional water table and is usually less than 10 ft thick (Baedecker and others, 1991; Gibs and others, 1993). Except in areas where leakage occurs, contaminant flow is predominantly horizontal with a slight downward component, possibly in response to recharge. The downgradient extent of the plume is unknown because it extends beyond the monitoring wells (a maximum distance of 80 ft from well DEP-1).

Although the plume in the regional aquifer forms downgradient from the contaminant source, it has variegated appearance. Zones of highly contaminated water and slightly contaminated water alternate across the plume. The submerged vapor probes and wells used for ground-water sampling are screened at different depths and were designed for sampling water from discrete 6-in. to 24-in. intervals of
Figure 4. Change in location of 2-milligram-per-liter concentration contour for total benzene, toluene, ethylbenzene, o-xylene, m-xylene, and p-xylene (BTEX) at a depth of 11 to 15 ft below land surface in the perched-water zone at the Galloway Township research site from July 1990 to April 1991. (Concentrations shown are in milligrams per liter. 1990 data from Baedecker and others, 1991; 1991 data from M.J. Baedecker and I.M. Cozzarelli, U.S. Geological Survey, written commun., 1993.)
Figure 5. Concentrations of total benzene, toluene, ethylbenzene, o-xylene, m-xylene, and p-xylene (BTEX) at an altitude of 33 to 35 feet in the regional aquifer at the Galloway Township research site in January 1990, July 1990, and April 1991. (Concentrations shown are in milligrams per liter. 1990 data from Baedecker and others, 1991; 1991 data from M.J. Baedecker and I.M. Cozzarelli, U.S. Geological Survey, written commun., 1993.)
the aquifer. Cozzarelli (1993) has demonstrated significant vertical heterogeneity in hydrocarbon concentration over short vertical distances. Radial flow around well DEP-1 could account for some of the observed contaminant distribution; however, determination of flow rates and flow directions is difficult as a result of steeper vertical gradients and lower hydraulic conductivities in the vicinity of this well than elsewhere at the site. The observed contaminant distribution also could be attributed to natural or borehole-induced leakage in the vicinity of vapor well VW-9. Another possibility is that separate-phase gasoline is trapped beneath the clay stringers and moves in response to changing flow directions. All these possibilities are currently being investigated.

Hydrologic conditions at the site also control the distribution of inorganic constituents used in microbially mediated oxidation-reduction reactions. Microbially mediated reactions identified at the site include aerobic respiration, denitrification, nitrate reduction, sulfate reduction, and iron reduction (Baedecker and others, 1991; Cozzarelli and others, 1991; Cozzarelli, 1993). Oxygen, nitrate, and sulfate are supplied to the plume in the perched-water zone by vertical percolation of recharge and reach the plume in the regional aquifer by horizontal flow (Cozzarelli and others, 1991). At the base of the perched-water plume, in an area of low rates of ground-water flow and high concentrations of hydrocarbons, oxygen and nitrate have been depleted and sulfate and iron reduction are the main biodegradation processes (Cozzarelli, 1993). At the edges of this plume, where recharge mixes with contaminated water, aerobic respiration, nitrate reduction, and denitrification occur. In the regional-aquifer plume, lower concentrations of oxygen and nitrate and higher concentrations of ammonia than those in uncontaminated water indicate that aerobic respiration, denitrification, and, possibly, nitrate reduction are the main biodegradation processes. On occasion, anoxic zones have formed in the regional-aquifer plume. This may be related to the rate of contaminant input and the length of time that one ground-water flow direction has been maintained. Changes in flow direction facilitate mixing of contaminants and oxygenated water and may preclude the formation of anoxic zones.

Water-chemistry data show that the geochemical environment in the regional aquifer is less stable than that in the perched-water zone (Baedecker and others, 1991). Reduced chemical species, such as reduced iron and hydrogen sulfide, are produced in anoxic environments and typically are not stable in oxygenated water. Leakage of anoxic perched water to the regional aquifer, either at well DEP-1 or other locations, may explain some of the instability. Also, anoxic zones may form at different locations in the regional aquifer at various times, depending on the recent stability of the regional flow direction.

**SUMMARY**

The USGS began investigations in 1988 at a site in Galloway Township, New Jersey, at which ground water had been contaminated by gasoline leaking from an underground storage tank. Sediments at the site, which is located in the New Jersey Coastal Plain, consist of horizontal layers of sand and clay. The two uppermost units of the ground-water-flow system, the perched-water zone and the unconfined regional aquifer, each contain a plume of gasoline-contaminated ground water. The areal extent and thickness of the perched-water zone varies with precipitation. The clay stringers that are responsible for the perching appear to be relatively impermeable in the northwestern part of the research site and leaky in the southeastern part. Monitoring well DEP-1, installed prior to USGS investigations, provides a conduit for water to flow down from the perched-water zone to the regional aquifer. The general direction of flow in the regional aquifer usually is to the east, but the direction varies from slightly north to east to east-southeast. Hydraulic gradients are less than 0.05, and estimates of average horizontal linear flow velocities range from 0.04 to 0.36 ft/d. Elevated water levels in well DEP-1 indicate that directions and rates of ground-water flow near this well vary significantly from regional flow directions.

Gasoline as a separate-phase liquid has been detected in only two places: in the regional aquifer in well DEP-1 and in the perched-water zone near the location of the exhumed tank. Dissolved-hydrocarbon contamination in the perched-water zone consists of a stable elliptical plume about 80 ft long and 40 ft wide in the 11 to 14 ft depth interval. Ground-water flow rates are very low where contaminants currently reside in the perched-water zone. Hydrocarbon contamination in the regional aquifer was downgradient from well DEP-1. The location of the contaminant plume varied with changes in ground-water flow directions. The thickness of the plume in the regional aquifer usually is
less than 10 ft, and hydrocarbon-contaminant flow is predominantly horizontal. The concentration of total aromatic hydrocarbons decreased downgradient, in part as a result of dilution, dispersion, and biodegradation. Hydrocarbon degradation is affected by the rate of movement of organic and inorganic chemical species in the ground water. Natural attenuation mechanisms are significant throughout the site and account for many of the observed changes in water quality.

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Biogeochemical Fate of Organic Acid Metabolites Produced During the Microbial Degradation of Hydrocarbons in Ground Water

By Isabelle M. Cozzarelli and Mary Jo Baedecker

Abstract

A combined field and laboratory study of low-molecular-weight organic acids was undertaken to improve an understanding of the distribution of organic acids and the geochemical parameters that influence the prevalence of these compounds in ground water of a shallow aquifer contaminated with gasoline, in Galloway Township, New Jersey. The degradation of aromatic hydrocarbons from gasoline occurred in situ by oxidation-reduction reactions mediated by bacteria. The important reactions were aerobic degradation and reduction of nitrate, sulfate, and Fe(III). Temporal and spatial shifts in the biogeochemical reactions occurred in response to changes in hydrogeochemical conditions in the aquifer.

Low-molecular-weight aliphatic, aromatic, and alicyclic organic acids were associated with hydrocarbon degradation in oxygen-depleted zones of the aquifer. Laboratory microcosm experiments demonstrated that the biogeochemical fate of specific organic acids observed in ground water varied with the structure of the acid and the availability of electron acceptors. Benzoic and phenylacetic acid were degraded by the indigenous aquifer microorganisms when nitrate was supplied as an electron acceptor. Aromatic acids with two or more substituents on the benzene ring persisted under nitrate-reducing conditions. Organic acids produced during hydrocarbon degradation participate in processes such as metal complexation, sorption, and mineral dissolution; thus, understanding the biogeochemical fate of organic acids is essential to predicting the geochemical evolution of shallow aquifers containing degradable organic compounds.

INTRODUCTION

Aromatic hydrocarbons are frequently reported in anoxic subsurface environments (for example, Reinhard and others, 1984; Barker and others, 1986; Baedecker and others, 1993; Elgahhouse and others, 1993). In these environments, anaerobic degradation is an important attenuation process. The degradation of monoaromatic hydrocarbons has been demonstrated to occur in the absence of oxygen by a variety of microbially mediated reaction pathways, including nitrate reduction (Kuhn and others, 1988; Major and others, 1988; Hutchins and others, 1991), iron reduction (Lovley and Lonergan, 1990), sulfate reduction (Edwards and Grbic'-Galic', 1992; Haag and others, 1991), and methanogenesis (Wilson and others, 1986; Grbic'-Galic' and Vogel, 1987). As a result of these degradation processes, oxidized organic compounds, such as low-molecular-weight (LMW) organic acids, are formed. A variety of metabolic intermediates, including aromatic, aliphatic, and alicyclic organic acids, phenols, and aldehydes, have been identified in laboratory experiments during the anaerobic microbial oxidation of petroleum hydrocarbons (Grbic'-Galic' and Vogel, 1987; Kuhn and others, 1988). The few reports of LMW organic acids in shallow aquifers contaminated with petroleum products provide documentation that these compounds are associated with the in situ anaerobic degradation of aromatic hydrocarbons (Cozzarelli and others, 1990,1991; Wilson and others, 1990; and Godsy and others, 1992).

Organic acids are more geochemically reactive than the hydrocarbon precursors. Although there is little understanding of the importance of sorption of simple organic acids onto aquifer sediments, the sorption of these polar compounds is

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known to occur onto oxide surfaces (for example, Kummert and Stumm, 1980), clay surfaces (Yariv and others, 1966), and organic coatings on mineral surfaces of marine sediments (Sansone and others, 1987). Organic acid anions also can form complexes with metals in solution (Sposito, 1989) and may thus facilitate the transport of dissolved metals in ground water.

Although organic acids may contribute significantly to the total organic carbon pool, little is known about the distribution and fate of LMW organic acids in ground-water environments. It is apparent that the transformation of aromatic hydrocarbons to more soluble, and potentially more reactive, intermediates may have significant implications to modeling the geochemical effects of organic solutes in ground water and the implementation of bioremediation technologies.

The research described in this paper is part of a larger ongoing study of the fate of LMW organic acids, produced during microbial degradation of aromatic hydrocarbons, in aquifers contaminated with petroleum products (Cozzarelli, 1993; Cozzarelli and others, 1990, and 1994). The purpose of this paper is to document how the distribution of organic acids in a shallow Coastal Plain aquifer contaminated with gasoline is affected by the availability of electron acceptors in the ground water. Specifically, the prevalence and type of dissolved organic acids in the ground water are related to temporal changes in the concentrations of nitrate in the aquifer. The field observations are compared to laboratory microcosm experiments constructed with aquifer sediment in which nitrate was added as an electron acceptor.

FIELD SITE

The field site is in Galloway Township, New Jersey, 10 mi west of Atlantic City. An underground storage tank on a farmer’s property leaked, resulting in the accumulation of pockets of a separate gasoline phase in the saturated and unsaturated zones of this shallow aquifer (Fischer and others, 1991). The aquifer is in surficial sediments of the Bridgeton Formation, described as fluvial feldspathic deposits (Owens and Minard, 1979) of the Atlantic Coastal Plain. The upper 20 ft of soil at the site is predominately fine- to medium-grained sand with iron-oxide coatings and discontinuous clay lenses and coarse-grained sand lenses throughout. Below a depth of 20 ft, coarse-grained sand predominates. At approximately 11 to 15 ft below land surface, a clayey-sand layer contains 1- to 3-in.-thick, dense, clay lenses that have a low hydraulic conductivity (Fischer and others, these proceedings). Due to the presence of the clayey layer, a perched water table is present above the water table aquifer beginning at about 10 ft below land surface. The water table fluctuated between approximately 14-17 ft below land surface during the period June 1989 - April 1991.

METHODS

Ground-Water Sampling.—Water samples were collected seven times over a 2-year period between June 1989 - April 1991. For this study, ground-water samples were collected from stainless-steel probes installed at site VW9 as described previously (Cozzarelli and others, 1991; Fischer and others, 1991). Samples were collected from 10.7, 12.5, 15.5, 18 and 22 ft below land surface, in both the perched and regional water zones. The areal distribution of hydrocarbon contaminants and unstable constituents at this site have been described by Baedecker and others (1991).

Water samples were analyzed for geochemical constituents that are important reactants, intermediates, or end products involved in the degradation of the dissolved hydrocarbons. Redox-sensitive constituents, including dissolved organic carbon (DOC), bicarbonate (HCO₃⁻), oxygen (O₂), ammonia (NH₄⁺), hydrogen sulfide (H₂S), ferrous iron (Fe²⁺), and methane (CH₄), were analyzed as described in Baedecker and Cozzarelli (1992). Nitrate and sulfate were analyzed on filtered (0.4 μm) samples by ion-exchange chromatography. Water samples for hydrocarbon analyses were collected and analyzed using a liquid-liquid extraction technique as described by Phinney and Cozzarelli (these proceedings). Samples for analysis of organic acids were collected and analyzed by extraction with diethyl ether and quantified by gas chromatography with flame-ionization detection and gas chromatography/mass spectrometry (Cozzarelli, 1993).

Microcosm Experiments.—To determine the biodegradability of selected aromatic organic acids found in ground water contaminated with gasoline hydrocarbons, microcosm experiments were conducted with nitrate added as electron acceptors. Sediment was collected for the microcosm experiments from the anoxic perched-water zone at a location 5 ft west of site VW9 in April 1991 (fig. 1). The cores were opened in a nitrogen (N₂)-filled glove bag at the field site and transferred to cleaned and sterilized glass jars. The jars were topped off with anoxic ground water collected at site VW9 at 12.5 ft below land surface (VW9-12.5) to minimize any headspace and kept on ice for transport to the laboratory. Twelve jars of sediment and an additional 2.5 L of water from VW9-12.5 were collected for use in the construction of the microcosms.
The microcosms were constructed and solutions prepared in a N₂-filled glove bag in the laboratory. Approximately 40 g of sediment from the field and 40 mL of organic-acid solution made with ground water from site VW9-12.5 were added to each 60 mL BOD bottle. Five organic acids were added to the ground water for all the experiments to yield a concentration of approximately 0.05-0.20 mM of each compound. The acids added were benzoic acid (added as sodium benzoate), ortho-toluic acid, phenylacetic acid, 3,4-dimethylbenzoic acid, and 2,4,6-trimethylbenzoic acid. Nitrate was added to the organic acid solution in sufficient quantity (30 mM) such that the concentration would not limit degradation reactions. The pH of the organic acid solutions was adjusted (with 1 normal potassium hydroxide) to 6.0, the pH value measured at site VW9-12.5 in the field when ground-water samples were collected. The degradation intermediates and end products produced during the incubation period were monitored at intervals of 1, 2, 4, 8, 16, and 32 days.

RESULTS AND DISCUSSION

Small-scale spatial and temporal changes in biogeochemical reactions at site VW9 resulted in significant vertical heterogeneity of chemical constituents in the aquifer. The concentrations of aromatic hydrocarbons, organic acids, and electron acceptors exhibited similar vertical distribution patterns throughout 1990 (Cozzarelli and others, 1991). Oxygen and nitrate were depleted in the shallow (10.7 ft below land surface) and deeper part of the perched water (12.5 and 15.5 ft below land surface). Cozzarelli and others (1991) reported that in the deeper part of the perched water sulfate reduction and iron reduction resulted in a decrease in sulfate concentrations and an increase in the concentrations of Fe²⁺ in the ground water. The highest concentrations of hydrocarbons and organic acids were found at these depths.

Changes were observed, however, in the distribution of electron accepting species in April 1991 (fig. 2 A,B). These changes result, in part, from changing hydrologic conditions at the site. Oxygen, nitrate, and
Figure 2. Concentrations of electron accepting species: A. NO$_3^-$ and B. SO$_4^{2-}$, as a function of depth below land surface, in ground water at site VW9 in February 1990 and April 1991.
sulfate in the shallow perched water (10.7-ft depth) are supplied by vertical recharge from precipitation events, whereas, at greater depths, these electron acceptors are also supplied by mixing with ground water originating from recharge areas upgradient of the site. Low-hydraulic-conductivity layers that form the base of the perched-water zone may inhibit mixing, thereby limiting the supply of electron acceptors. The higher nitrate and sulfate concentrations in the upper perched water in 1991 (fig. 2) indicate that nitrate and sulfate reduction by anaerobic respiration were not limited by availability of electron acceptors. The increased availability of electron acceptors is probably a result of a combination of increased recharge in the spring of 1991 and a decrease in degradable hydrocarbons in the ground water (Cozzarelli, 1993).

The changes in concentration of specific classes and structures of organic acids over time in the ground water at site VW9 provide insight into the persistence of certain organic acid structures in the presence of different electron acceptors. In the presence of nitrate in the shallow perched water, aliphatic organic acids were consumed at a rapid rate and did not accumulate in the ground water (Cozzarelli, 1993). This observation was in contrast to the observation of increased concentrations of aliphatic organic acids in the methanogenic zones of aquifers contaminated with petroleum products (Cozzarelli and others, 1994). Under the nitrate-reducing conditions of the shallow perched water, however, aromatic acids, as a class, were persistent.

The persistence of individual aromatic acids is different--largely dependent on their structures--in the perched water where nitrate reduction and denitrification were occurring (fig. 3). Because the metabolic intermediates of hydrocarbon degradation are both produced and consumed by microbiological processes, rates of degradation of the organic acids cannot be inferred from the changes observed in ground water over time. However, the relative persistence of the different compounds indicates that the simple aromatic acids, benzoic acid and phenylacetic acid, are either degraded more quickly when nitrate is available as an electron acceptor or that they were not produced as extracellular intermediates during hydrocarbon degradation under nitrate-reducing conditions. The organic

GALLOWAY SITE VW9, 10.7 FT BELOW LAND SURFACE

- **BENZOIC ACID**
- **PHENYL ACETIC ACID**
- **o-TOLUIC**
- **3,4 DIMETHYLBENZOIC ACID**
- **2,4,6 TRIMETHYLBENZOIC ACID**
- **ERROR BARS**

**Figure 3.** The concentrations of individual aromatic organic acids: benzoic acid, phenylacetic acid, ortho-toluic acid, 3,4-dimethylbenzoic acid, and 2,4,6-trimethylbenzoic acid in the ground water at site VW9 in February 1990 and April 1991 in the perched water at 10.7 feet below land surface.
acids with more substituents, ortho-toluic acid, 3,4-dimethylbenzoic acid, and 2,4,6-trimethylbenzoic acid, increase in concentration under the same conditions. Studies by other investigators have found that slight changes in the number or type of substituents on the aromatic ring causes compounds to be more or less resistant to biological degradation (see, for example, Horowitz and others, 1982; Berry and others, 1987).

The results from the microcosm experiments in which NO\textsubscript{3}\textsuperscript{-} was added as a potential electron acceptor clearly establish that NO\textsubscript{3}\textsuperscript{-} reduction is coupled to the biological degradation of the simplest aromatic acids, benzoic acid and phenylacetic acid (fig. 4). Complete mineralization occurs, as evidenced by the loss of organic acids and production of bicarbonate in the microcosms over time. Although initiation of benzoic acid degradation appeared to occur first, the degradation of phenylacetic acid was observed before benzoic acid was depleted. Between days 16 and 32, after the benzoic acid was depleted, 0.093 mM of phenylacetic acid was degraded. For complete oxidation of that amount of organic carbon, 0.74 mM of HCO\textsubscript{3}\textsuperscript{-} should have been produced. This amounts to a transfer of 36 electrons. Over this time period, an increase of 0.50 mM of HCO\textsubscript{3}\textsuperscript{-} was actually measured, indicating that 33 percent of the CO\textsubscript{2} went into biomass, assuming there were no losses of aqueous CO\textsubscript{2} from the system. Alternatively, some carbon could be present as metabolic intermediates; however, none were detected during the organic acid analyses. If the oxidation of phenylacetic acid was coupled to nitrate reduction to NH\textsubscript{4}\textsuperscript{+}, 0.42 mM of NO\textsubscript{3}\textsuperscript{-} would need to be reduced to balance the electrons released. If, on the other hand, denitrification was occurring, 0.67 mM of NO\textsubscript{3}\textsuperscript{-} would be reduced. The actual amount of NO\textsubscript{3}\textsuperscript{-} reduced was 1.06 mM, indicating that the reduction of nitrate may have been coupled to the oxidation of other organic compounds in the microcosms as well.

In a study of the degradation of benzoic acid and phenylacetic acid by a sulfate reducer, Desulfosarcina strain DSU3, Sembiring and Winter (1989) observed that both substrates were utilized simultaneously when the concentrations of both compounds were less than 3.5 mM. They also observed that benzoic acid degraded first when in the presence of phenylacetic acid--an observation consistent with the results of the microcosm experiment presented here in which NO\textsubscript{3}\textsuperscript{-} was added as an electron acceptor. However, in contrast to the current study, where no aliphatic acids were detected in the microcosms, Sembiring and Winter

![Graph](image-url)

**Figure 4.** The concentration of nitrate, bicarbonate, benzoic acid and phenylacetic acid as a function of time (in days), in the microcosm experiments in which nitrate was added as an electron acceptor.
(1989) found significant accumulation of acetic acid during the degradation of benzoic acid. This difference may indicate that the more reducing conditions, under which sulfate reduction occurs, result in the accumulation of acetate whereas nitrate-reducing conditions do not.

The lack of any degradation of the higher alkylated benzoic acids in the microcosms with nitrate added indicates that they were resistant to biodegradation under the conditions employed in the experiments. The observation, that the degradation of the organic acids by aquifer microorganisms is structure specific, is consistent with other reports of selective degradation of aromatic compounds in the literature (for example, Eganhouse and others, 1987 and 1993; Kuhn and others, 1989; Evans and others, 1991; Haag and others, 1991). Several of the pathways proposed for anaerobic degradation of aromatic compounds require substituent removal before ring reduction and ring cleavage. The magnitude of the activation energy required to remove substituents depends upon chain length and position of the substituent. In particular, aromatic compounds with substitutions at the ortho position are more stable than aromatic compounds with substitutions at other positions.

**SUMMARY**

The fate of organic acids in a shallow aquifer contaminated with gasoline is controlled by a complex interplay between microbial degradation processes and geochemical and hydrologic changes in the aquifer. Organic acids were found to be associated with hydrocarbon degradation in oxygen-depleted zones of the aquifer. The organic acid pool changed in composition and concentration over time and in space as the availability of electron acceptors changed. The alkylbenzoic acids with two or more functional groups appeared to be the most persistent under a range of hydrogeochemical conditions. The availability of nitrate—nitrate in particular, nitrate from infiltrating water—appeared to be an important geochemical parameter that resulted in low concentrations of simple aromatic acids in ground water. In contrast, alkylbenzoic acids with a greater number of functional groups were more persistent under nitrate-reducing conditions.

Laboratory microcosm experiments, designed to simulate field geochemical conditions, demonstrated that the biogeochemical fate of specific organic acids observed in the ground water varied depending on the structure of the acid and the availability of electron acceptors. The addition of nitrate as an electron acceptor enhanced the microbial degradation of benzoic acid and phenylacetic acid that were added to the experiments as substrates.

The results presented here, combined with our previous studies of organic acids in shallow aquifers (Cozzarelli and others, 1991 and 1994) indicate that the types and concentrations of LMW organic acids identified in ground water contaminated by petroleum hydrocarbons are related to the geochemical conditions under which the degradation of the organic compounds occurred.

**REFERENCES**


Method for Estimating the Rate of Microbial Degradation of Hydrocarbons Associated with Bioventing at a Gasoline-Spill Site in Galloway Township, New Jersey

By Matthew A. Lahvis¹, Arthur L. Baehr¹, and Jeffrey M. Fischer¹

Abstract

Bioventing is the enhancement of microbial degradation caused by the delivery of atmospheric oxygen to aerobically biodegradable contaminants in the subsurface through vapor-extraction remediation. Simulation of the redistribution of oxygen and carbon dioxide in the unsaturated zone following a period of vapor extraction provides a method for estimating the rate of microbial degradation of hydrocarbons. Rebound vapor-concentration data are used to calibrate a diffusive-transport model developed to quantify gas fluxes and the degradation rate. The resulting rates are indicative of the upper limit of aerobic degradation that can occur during or immediately after vapor extraction, when oxygen availability exceeds microbial utilization. Microbial degradation of is a significant hydrocarbon fate at a gasoline-spill site in Galloway Township, New Jersey.

INTRODUCTION

The distribution and fate of hydrocarbons in the subsurface depends on their tendency to dissolve in ground water, volatilize to the atmosphere, adsorb to sediment material, or undergo biochemical transformations. Energy-intensive methods to treat physically or remove the contaminant typically are hampered by the transport characteristics of the sediment and the physiochemical properties of the hydrocarbon (its solubility, vapor pressure, and sorption potential). Restoration of a hydrocarbon-contaminated aquifer may occur naturally, however, through microbial degradation processes that molecularly transform hydrocarbons to harmless end-products. This mechanism, as well as other natural attenuating mechanisms, such as volatilization to the atmosphere, commonly are the only viable means of remediation. Engineered attempts at remediation may be less effective in the field than in theory, especially at hydrogeologically complex contamination sites. Quantification of site-specific degradation rates may therefore be beneficial to regulators and environmental engineers challenged by the escalating costs of cleanup and faced with the consequences of partial remediation or no-action scenarios. In Wisconsin, for example, natural biodegradation must now be considered as a remediation option at hydrocarbon-contaminated sites (Wisconsin Department of Natural Resources, 1993).

Bioventing is the enhancement of microbial degradation caused by delivery of atmospheric oxygen to aerobically biodegradable contaminants in the subsurface through vapor-extraction remediation. Microbial degradation reactions at the ground-water table results in an accumulation of carbon dioxide (CO₂) and a reduction in oxygen (O₂) in the gas phase of the overlying unsaturated zone. During vapor extractions at a gasoline-spill site at Galloway Township, New Jersey (fig. 1), near-atmospheric gas-phase concentrations of CO₂ and O₂ are generated throughout the unsaturated zone. When vapor extraction is terminated, the subsequent redistribution, or rebound, of these gases in the unsaturated zone overlying the area of ground-water contamination provides a signature of microbial degradation as it occurred during vapor extraction. The degradation rate is quantified by calibrating a diffusive-transport model to rebound vapor-concentration data. As outlined by Baehr and others (1991), knowledge of the composition of unsaturated-zone gas coupled with transport modeling can be used to estimate degradation...
Figure 1. Map of the research site at Galloway Township, New Jersey, showing location of Vapor Well 9 (VW9).

- Nested vapor probes
- U.S. Geological Survey ground-water observation well
- Former tank
- New Jersey Department of Environmental Protection ground-water observation well
- Multilevel ground-water sampler
- Neutron probe access
- Thermistor nest
- Vapor-extraction well
- VW9 Vapor probe number
rates under unremediated conditions. This problem was addressed by Fischer and others (1992) and Lahvis (1993). This paper describes the application of the method of Baehr and others (1991) to obtain a site-specific upper-bound estimate of the degradation rate when oxygen transport is not a limitation on aerobic degradation.

FIELD METHODS

Unsaturated-zone gas samples were collected from a network of vapor probes (methods discussed by Fischer and others, 1991) and their composition determined by using gas chromatography (Baker and others, 1991). Samples of perched water were collected from submerged vapor probes with a peristaltic pump and analyzed for dissolved hydrocarbons, dissolved oxygen, alkalinity, and pH. The distribution of organic and inorganic constituents in the ground water is described further by Baedecker and others (1991). Unsaturated-zone-sediment samples were collected with a split-spoon sampler and analyzed for total porosity and moisture content. Core samples were used to map the unsaturated-zone stratigraphy. The site geology is discussed further by Fischer and others (1991) and Fischer, Smith, and Baehr (1996). Some undisturbed sediment cores were used directly in laboratory column experiments to measure the effective diffusion coefficient (Fischer, Baker, Lahvis, and Baehr, 1996), a parameter required for vapor-transport modeling. A nest of thermistors and neutron probes was used to obtain additional depth-dependent temperature and moisture-content data, respectively, to help assess the diffusive-transport characteristics of the unsaturated-zone sediments.

Synoptic vapor- and ground-water sampling was conducted at the Galloway Township site to document conditions at the site prior to applying vapor extraction (Fischer and others, 1991). The distribution of CO₂ and O₂ in the unsaturated zone is presented by Baehr and others (1991). High concentrations of dissolved hydrocarbons were present in the perched (10 feet below land surface), particularly near Vapor Well 9 (VW9) (Baedecker and others, 1991), but were not detected in the overlying unsaturated zone except in a small region near the former location of the exhumed gasoline tank (Fischer, Smith, and Baehr, 1996). This observation indicates the presence of thin microbially active zone near the perched water table, where the rate of hydrocarbon degradation exceeds the rate of hydrocarbon volatilization to the overlying unsaturated zone.

MODEL APPLICATION

The diffusive-transport model developed to quantify microbial degradation in porous media implements the following one-dimensional analytical solution to the diffusion equation under the assumption of unsaturated-zone homogeneity:

\[ a_k \frac{\partial G_k}{\partial t} = D_k \frac{\partial^2 G_k}{\partial z^2} \]  

where the subscript k indicates that the equation applies to either CO₂ or O₂, G_k (g/cm³) is the gaseous-phase concentration of the constituent, D_k (cm²/s) is the effective diffusion coefficient, a_k (unitless) is the storage coefficient, and L (cm) is the total length of the model domain. A homogeneous unsaturated zone implies that D_k and a_k are constant, which in turn implies that the physical properties of the porous medium (total porosity, moisture content, and tortuosity) are constant. Because all degradation is simulated through use of a boundary condition at the perched water table, CO₂ and O₂ transport are uncoupled. Equation 1 incorporates the following assumptions: equilibrium partitioning of the mass between the gaseous and aqueous phases, negligible adsorption, and no constituent sources or sinks.

This model was applied to simulate the redistribution of CO₂ and O₂ near VW9. Vapor-concentration data collected from vapor probes (VW9-6.0 and VW9-8.2 were used in the one-dimensional vapor-transport analysis. A conceptualization of the unsaturated-zone stratigraphy in the vicinity of VW9 is shown in figure 2. A high relative moisture content measured in the thin clay layer (unit #4), indicates that modeling the entire unsaturated zone as a uniform porous medium may be inappropriate. To account for this sharp discontinuity, the model domain was reduced to the three lowermost stratigraphic units (nos.1-3) and the clay was modeled as a third-kind
boundary, analogous to a leaky confining unit, as follows:

$$-D_k' \frac{\partial G_k}{\partial z} = -D_k' \left( \frac{G_{k_{\text{aim}}}}{b'} - G_k \right), \text{ at } z = L$$  \hspace{1cm} (2)

where $D_k'$ (cm$^2$/s) is the effective diffusion coefficient of the clay layer; $b'$ (cm) is the clay-layer thickness; $L$ (cm) is the length of the model domain; and $G_{k_{\text{aim}}}$ (g/cm$^3$) is the constants concentration of the constituent on the opposite site of the clay layer, typically designated as the atmospheric concentration.

The lower boundary corresponds to the top of the capillary zone, which is defined by a sharp gradient in the moisture content. An analytical solution was obtained for two boundary-condition cases: (1) a constant flux, $J_k$ (g/cm$^2$/s); and (2) a constant concentration, $G_k$ (g/cm$^3$), modeled as follows:

$$J_k (z) = -D_k \frac{\partial G_k}{\partial z}$$  \hspace{1cm} (3)

$$G_k (z) = G_0 \text{ case (2) at } z = 0.$$  \hspace{1cm} (4)

The constant-flux boundary condition implies constant substrate utilization, independent of transport in the unsaturated zone above, whereas the constant-concentration boundary condition implies time-dependent degradation, directly influenced by unsaturated-zone transport. The boundary conditions mathematically span the range of microbial responses to unsaturated zone-transport, bracketing boundary-condition sensitivity.

The initial condition is specified as a linear piecewise interpolation through specified points as follows:

$$G_k (z, 0) = A_k (z)$$  \hspace{1cm} (5)

The solution to (1) subject to the boundary conditions (2), (3), or (4), and the initial condition (5) is obtained by applying the separation-of-variables solution technique as follows:

$$G_k (z, t) = v (z, t) + K (z)$$  \hspace{1cm} (6)

where $v(z,t)$ is the transient component of the solution, and may be written as:

$$v (z, t) = \left\{ \sum_{n = 0}^{\infty} T_n (t) \phi_n (z) \right\}$$  \hspace{1cm} (7)

where:

$$T_n (t) = C_n \exp \left( -\lambda_n D_k t \right)$$

$$\phi_n = \cos \sqrt{\lambda_n} z \text{ for case 1, or}$$

$$\phi_n = \sin \sqrt{\lambda_n} z \text{ for case 2.}$$

In general,

$$C_n = 2 \int_0^L \left[ A_k (z) - K (z) \right] \phi_n dz$$

where $A_k (z)$ is the initial condition comprised of $m$ components, given by:
Figure 3. Analytical model calibration to summer 1991 carbon dioxide vapor-concentration data with application of the constant carbon dioxide flux boundary condition.

\[ A_k(z) = \sum_{i=1}^{m} M_i \frac{O}{k_i} z + B_k \frac{O}{k_i} \]  

and \( K(z) \) is the steady state solution defined as:

\[ K(z) = \left( \frac{J_k}{D_k} \right) + \left[ k \left( \frac{h'}{D_k} + \frac{L}{D_k} \right) + G_{k_{atm}} \right] \]  

\[ (8a) \]

\[ K(z) = \left[ \frac{(G_{k_n} - G_{k_{atm}})}{L + \frac{D_k}{D_k} h'} \right] z + G_{k_n} \]  

\[ (8b) \]

For each case, the constants \( C_n \) are defined more specifically as:

\[ C_n = \frac{2}{L} \sum_{i=1}^{m} \left\{ \frac{M_i}{\lambda_n} \left[ \cos L \sqrt{\lambda_n} + L \sqrt{\lambda_n} \sin L \sqrt{\lambda_n} - 1 \right] + \frac{B_i}{\lambda_n} \sin L \sqrt{\lambda_n} \right\} \]  

for case 1, or
\[ C_n = \frac{2}{L} \sum_{i=1}^{m} \left\{ \frac{M_i}{\lambda_n} \left[ \sin L \sqrt{\lambda_n} + L \sqrt{\lambda_n} \cos L \sqrt{\lambda_n} \right] + \left[ \frac{B_i}{\lambda_n} \cos L \sqrt{\lambda_n} - 1 \right] \right\} \text{ for case 2,} \]

where:

\[ M_i = M^{o}_{k_i} + \frac{J_k}{D_k} \text{ for case 1, or } M_i = M^{o}_{k_i} - \left( \frac{G_{k_{\text{ini}}} - G_{k_{n}}}{L + \frac{D_k}{D_k'}} \right) \text{ for case 2, and} \]

\[ B_i = B^{o}_{k_i} - \left( J_k \left( \frac{b'}{D_k} + \frac{L}{D_k'} \right) \right) + G_{k_{\text{ini}}} \text{ for case 1, or } B_i = B^{o}_{k_i} - G_{k_{n}} \text{ for case 2.} \]

The eigenvalues (\( \lambda_n \)) in each case are determined numerically by the Newton-Raphson method and are given by:

\[ \tan L \sqrt{\lambda_n} = \frac{D_k'}{b'} \text{ for case 1, or } \tan L \sqrt{\lambda_n} = \frac{-D_k \lambda_n}{D_k'} \text{ for case 2.} \]

### RESULTS AND SUMMARY

For this analysis, the magnitude of the boundary condition (\( J_k \) and \( G_k \)) and the effective diffusion coefficients (\( D_k \) and \( D_k' \)) are determined by means of model calibration by using a least-root-mean-squares fit between measured and simulated rebound vapor-concentration data. Rebound vapor-concentration samples were collected over a 1,000-hour period after vapor extraction was terminated.

The relations among the rates of hydrocarbon degradation, carbon dioxide production, and oxygen consumption are defined under the assumption that aerobic degradation is the dominant microbial-degradation pathway and hydrocarbon mineralization is complete. (Baker and Baehr, 1996). The hydrocarbon-degradation rate in the perched water zone is then stoichiometrically related to the flux of \( \text{CO}_2 \) and \( \text{O}_2 \) in the unsaturated zone as follows:

\[ R_{\text{bio}} = \frac{J_k}{r_k} \]  \hspace{1cm} (9)

where \( R_{\text{bio}} \) ((g/cm\(^2\)/s) is the hydrocarbon-degradation rate, and \( r_k \) (unitless) is the stoichiometric mass constant relating the mass of \( \text{CO}_2 \) produced or mass of \( \text{O}_2 \) consumed to the mass of hydrocarbon degraded. Stoichiometric mass constants \( r_{\text{CO}_2} = 3.19 \) and 2.28 \<r_{\text{O}_2}\> \leq 3.32 were calculated for carbon dioxide and oxygen, respectively (Lahvis, 1993). Any agreement between the degradation rate calibrated by using \( \text{CO}_2 \) vapor-concentration data and the rate calibrated by using \( \text{O}_2 \) vapor-concentration data supports the hypothesis of complete hydrocarbon mineralization.

Results for calibration to the \( \text{CO}_2 \) rebound data obtained during summer 1991 with application of the constant-flux boundary condition (case 1) are illustrated in figure 3. A microbial degradation rate of \( R_{\text{bio}}=2.22\times10^1 \) ((g/cm\(^2\))/s) was calibrated at the degradation boundary. Similar estimates were obtained from other model calibrations (Lahvis, 1993). This rate can be extrapolated to a sitewide estimate of pure hydrocarbon degradation (\( R_{\text{bio}}=16.4 \) L/yr, or 4.33 gal/yr) by assuming a plume diameter of 1524 cm (50 ft) and an average hydrocarbon density of 0.77 g/cm\(^3\).

Calibrated estimates of the diffusion coefficient for the model domain (\( D_k \)) compared favorably to laboratory-based estimates (Baker, 1993; Lahvis, 1993). This agreement lends credibility to the estimate of flux, the other unknown parameter defined by model calibration.

In summary, the sitewide degradation-rate estimate, \( R_{\text{bio}}=16.4 \) L/yr, determined by means of model calibration to \( \text{CO}_2 \) rebound data collected...
during summer 1991, represents an upper bound of aerobic degradation that occurs during or immediately after vapor extraction when oxygen transport in the unsaturated zone is not a limitation. A similar rate estimate, $R_{bio} = 15.8 \text{ L/yr} (4.18 \text{ gal/yr})$, was obtained by calibrating a more comprehensive numerical transport model to the same data. The numerical model accounts for spatial variability in the diffusion and storage coefficients (Lahvis, 1993). The microbial degradation rate calibrated by using this approach indicates that microbial degradation of hydrocarbons is a significant process at the Galloway Township site, the rate of which exceeds the rate of volatilization into the atmosphere under unremediated conditions. This modeling approach provides regulators and environmental engineers with an ability to quantify the bioventing performance at other hydrocarbon-contaminated sites.

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Determination of Vapor-Phase Diffusion Coefficients for Unsaturated-Zone Sediments at a Gasoline-Spill Site in Galloway Township, New Jersey

By Jeffrey M. Fischer, Ronald J. Baker, Matthew A. Lahvis, and Arthur L. Baehr

Abstract

The rate of diffusion of gases through the unsaturated zone has been related to rates of microbial degradation of hydrocarbons at a gasoline-spill site in Galloway Township, New Jersey. The diffusion coefficient for the unsaturated porous medium is required to obtain rates of vapor movement from vapor-concentration measurements. Laboratory experiments were conducted on heterogeneous sediment cores to identify vapor-phase concentration profiles and vapor fluxes. A one-dimensional vapor-diffusion model based on the Stefan-Maxwell equations was used to calculate diffusion coefficients from these experiments. Diffusion coefficients obtained by using this method were smaller than those predicted by using the Millington-Quirk equation, and were particularly significant for clayey sediments. Use of the theoretically calculated diffusion coefficients to calculate vapor flux and biodegradation rates at the study site would have led to overestimates of these rates when compared to those determined by using the experimental method.

INTRODUCTION

Studies of diffusive transport in the unsaturated zone of hydrocarbon vapors and inorganic-gas constituents that are indicators of biodegradation are being conducted at a gasoline-spill site in Galloway Township, N.J. (Baehr and others, 1991; Baehr and Fischer, 1996; Baker and Baehr, 1996; Lahvis and others, 1996). Diffusion of gases through the unsaturated zone is controlled by the vapor-constituent concentration gradient and the diffusion coefficient. Unsaturated-zone concentration profiles can be measured (Baker and others, 1991; Fischer and others, 1991), whereas diffusion coefficients are determined by using some form of tracer experiment. The diffusion coefficient (D) of a vapor constituents in an unsaturated porous medium is commonly defined as follows:

\[ D = D_h \theta_a \tau, \]  

where

- \( D_h \) is the diffusion constant of the vapor constituent in a bulk gaseous phase identical to that in the unsaturated-zone atmosphere,
- \( \theta_a \) is the air-filled porosity, and
- \( \tau \) is the tortuosity of the vapor-filled pores.

\( D_h \) and \( \theta_a \) are measured independently of diffusion experiments. The tortuosity depends only on pore-space configuration and is independent of vapor constituents. A widely used empirical approximation for tortuosity is the Millington-Quirk equation (Millington and Quirk, 1961):

\[ \tau = \theta_a^{2/3} / \phi^2, \]  

where \( \phi \) is porosity.

This paper describes laboratory tracer experiments that were conducted on sediment cores from the Galloway Township research site. It describes and demonstrates the use of a one-dimensional model that was developed to estimate diffusion coefficients on the basis of the Stefan-Maxwell equations.

METHODS

Fickian diffusion is commonly assumed to be sufficient for calculating diffusive fluxes, or, if fluxes are known (as in a controlled experiment), for calculating tortuosity. Baehr and Bruell (1990) have shown that the Fickian assumption can lead to errors in estimated tortuosity values under certain conditions. This assumption can introduce substantial errors in subsequent calculations of biodegradation rates. A more rigorous approach for quantifying multicomponent vapor-phase diffusive transport in an unsaturated porous medium is to use the Stefan-Maxwell equation (Baehr and Bruell, 1990).
Four cores were collected from the study-site location shown in figure 1. The sampling location is the site of concurrent *in situ* biogradation studies (Lahvis and others, 1996) and sample collection for laboratory biogradation experiments (Baker and Baehr, 1996). Cores were collected in 3.6-cm-i.d., 61-cm-long aluminum tubes with a split-spoon sampler. Two of the four cores collected were used in laboratory vapor-diffusion experiments.

The column design used in the laboratory experiments is shown in figure 2. Cores were oriented vertically and a stainless-steel screen was attached to the bottom of the core liner to support the sediment. The tracer constituent is placed in a reservoir below the screen. For these experiments, pure liquid toluene was maintained in the reservoir. The liquid maintained a toluene-saturated airspace at the bottom of the core. If necessary, several centimeters of sediment were removed from the top of the column, and a cap was placed on the liner, creating an airspace. During the experiments, this space was purged continually with humidified gas (95 percent nitrogen and 5 percent oxygen, by volume). Purging with the sweep gas constantly removed vapor-phase toluene that had diffused through the column. Bracketing the column with toluene-saturated gas at the base and a sweep gas with a low toluene concentration at the top resulted in a vertical concentration profile in the sediment. Sampling ports were installed at about 9-cm intervals to determine this profile. Sampling ports consisted of 18-gauge stainless-steel syringe needles that were inserted through holes drilled in the core liner. The holes were sealed and the syringe needles were capped with syringe valves. Toluene concentrations were determined by using a gas chromatograph with a flame-ionization detector. Inorganic-gas concentrations (oxygen and carbon dioxide) were determined by using a gas chromatograph with a thermal-conductivity detector (Baker and others, 1991). Toluene flux at the top of the column was determined by multiplying the volumetric flow rate by hydrocarbon concentration in the sweep gas and dividing the result by the cross-sectional area of the column. When a steady vapor-phase composition, as indicated by an unchanging hydrocarbon profile, was reached in the column, vapor-concentration data were collected for use in model calibration. At the end of the experiments, the column was cut into 2-cm to 5-cm sections, and sediment lithology, porosity, and moisture content were determined.

A one-dimensional vapor-diffusion model was developed for analyzing laboratory column vapor-concentration and physical-property data to estimate tortuosity as a function of column depth. The model, an expansion of work by Baehr and Bruell (1990), incorporates the Stefan-Maxwell equations into a steady-state conservation-of-mass equation to define transport of each component of a multicomponent gas mixture in an unsaturated porous medium. The model has the ability to simulate one-dimensional vapor transport through a variably saturated porous medium that is heterogeneous with respect to porosity, moisture content, and the diffusion coefficient. Laboratory column vapor-concentration and physical-property data are simulated as a one-dimensional series of nodes. The model is calibrated by varying tortuosity values at nodes until the difference between observed and simulated constituent concentrations is minimized. Details of the model are presented in Baker (1993); additional uses of the model are presented by Baker (1993) and Baker and Baehr (1996).

The model requires data on vapor-phase constituents and porous-medium physical properties. Only steady-state conditions were considered in these simulations. Vapor-phase inputs include constituent concentrations and sample depths, as well as concentrations and fluxes of the constituents in the sweep gas. Porous-medium inputs include porosities and volumetric moisture contents. Initial estimates of tortuosity also are required; these were calculated by using Fick's law. Additional data on physical characteristics include atmospheric pressure, temperature, and sediment-column length.

The ability of the model to accurately estimate tortuosity was tested by using data reported in Baehr and Bruell (1990) for a homogeneous dry sand column. The reported tortuosity for benzene diffusion through the column was 0.566. The simulated concentration profile matched the reported profile and the estimated tortuosity for 13 nodes averaged 0.576, with a standard deviation of 0.073. This result indicated that the model can be used to produce accurate estimates of tortuosity.

**VAPOR-PHASE-DIFFUSION COEFFICIENTS**

Core-2, the first core from the Galloway Township site to be analyzed, came from a depth of 0.6 to 1.2 m. It contained nonlayered, fairly uniform sediments composed of approximately 30 percent clay, 25 percent silt,
Figure 1. Galloway Township gasoline-spill study site showing location where cores for laboratory experiments were obtained.
Figure 2. Column design for estimating tortuosity values of sediment cores. (Hydrocarbon reservoir and sweep-gas cap slip over core liner and are sealed in place with O-rings and lock nuts (not shown). Sediment level in core liner varied depending on amount of sample recovery. Vapor sample ports are spaced about 9 cm apart. Number of ports varied with the amount of sediment recovery. Sweep gas was 95 percent nitrogen and 5 percent oxygen. Hydrocarbon used in experiments was toluene.)
and 45 percent coarse- to fine-grained sand. Other physical properties of the core are listed in Table 1, in which estimated values of tortuosity from the simulations are compared to Millington-Quirk estimates. Simulated and actual vapor concentrations compare favorably, demonstrating a successful model calibration (Fig. 3). Values for tortuosity derived from simulations were consistently greater than 1.0 (an infeasible value) for the upper 10 cm of the sediment column. No such problems were encountered in similar experiments in which repacked sediments were used (Baker, 1993). Values greater than 1.0 probably indicate the

Table 1. Physical properties of core subsections and tortuosity values calculated by using the Millington-Quirk equation (theoretical) and those simulated with the model  
\[ \text{g/cm}^3, \text{grams per cubic centimeter; V/V volume per volume; --, no data; >, greater than; <, less than} \]  

<table>
<thead>
<tr>
<th>Sample Interval (cm)</th>
<th>Bulk Density (g/cm$^3$)</th>
<th>Total Porosity (V/V)</th>
<th>Air-filled Porosity (V/V)</th>
<th>Tortuosity (theoretical)</th>
<th>Tortuosity (simulated)</th>
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<tr>
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<td>0.311</td>
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<td>.234</td>
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<td>.149</td>
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<td>.217</td>
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<td>&lt;.001</td>
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<td>.126</td>
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Figure 3. Measured and simulated toluene concentration with depth for homogeneous sediments (core-2) and heterogeneous layered sediments (core-3).
presence of a short-circuited flow path in the disturbed part of the upper core. Nondiffusive flux through the upper part of the volume does not affect diffusive flux through lower parts of the column.

Core-3, the second core from the Galloway Township site to be analyzed, came from a depth of 1.5 to 2.1 m. It contained heterogeneous sediments with layers of sand, clay, and clayey sand (fig. 3). Physical properties of the layers are listed in table 1. Porosity and moisture-content values were assigned at layer interfaces to define layers in the model. Thus, values measured within a layer were entered at depths 1 cm above or below the interface to define the sediment discontinuity for the model. As for the previous core, estimated values of tortuosity were greater than 1.0 for the upper 15 cm of the column. No concentration gradient could be measured in the sand beneath the clay layers situated in the core at depths between 24.0 and 37.0 cm because the diffusion coefficient of the underlying sand was so much greater than that of the clays, which were effectively a “transport bottleneck.” Without a concentration gradient, it was not possible to calculate tortuosity in this layer; a separate laboratory experiment would need to be conducted on the sand alone to obtain this estimate. Estimates of tortuosity for the part of the core that was amenable to analysis with the model ranged from 0.001 to 0.033 (table 1), and simulated and actual vapor concentrations matched closely (fig. 3). The lower tortuosity value is for a thin clay lens at a core depth of 24 to 26.5 cm. Tortuosity values for the remaining layers were similar to those for core-2 because the physical properties of the sediment were similar.

Simulated tortuosity values for both cores generally were 2 to 20 times less than those predicted by using the Millington-Quirk equation (table 1) probably because the Millington-Quirk equation incorporates the assumption that the particles were spherical and the sediments contain considerable amounts of clay. Use of tortuosity values estimated from the Millington-Quirk equation to calculate vapor fluxes would have caused an overestimation of vapor fluxes at the site by an order of magnitude. Therefore, subsequent calculations of biodegradation rates at the site based on calculated vapor-transport values also would yield seriously overestimated values.

Although values of tortuosity calculated for cores in the laboratory are believed to be more representative of in situ conditions than theoretically obtained estimates, some uncertainty exists. Some sediment compaction probably occurred during sampling and while the cores were standing vertically in the lab. Further, moisture redistribution probably occurred as well. Compaction would cause tortuosity values to decrease and moisture redistribution would cause it to increase near the top of the core and decrease toward the bottom.

Although the model accurately simulated measured vapor concentrations, several concerns are being addressed. These include the sensitivity of tortuosity estimates to nodal spacing, and ways to reconcile differences in the vertical spacing of measured values (vapor concentration, moisture content, and porosity) and predicted values (vapor concentration and tortuosity). Also, to conserve computing time, an improvement in the algorithm used to minimize the difference between observed and simulated vapor concentrations may be made.

**SUMMARY**

Diffusion coefficients are required to quantify vapor fluxes through the unsaturated zone when the vapor-concentration distribution is known. Sediment cores from the unsaturated zone at the Galloway Township gasoline-spill research site were used to illustrate a method developed to obtain diffusion coefficients. The method involves the use of laboratory tracer experiments and the application of a one-dimensional model based on the Stefan-Maxwell equations. Physical-property data and vapor-concentration data from homogeneous and heterogeneous cores were used to successfully estimate tortuosity. Tortuosity in the upper part of the cores could not be estimated, however, possibly as a result of short-circuited flow through disturbed sediments. Tortuosity in the lower part of the layered core could not be simulated because concentration gradients could not be measured. Calculated tortuosity values ranged from 0.001 for a clay layer to 0.033 for clayey sands. Simulated tortuosity values were about 2 to 20 times less than those predicted by using the Millington-Quirk equation. Use of tortuosity values estimated by using the Millington-Quirk equation would have resulted in the overestimation of vapor fluxes at the site and the overestimation of biodegradation rates based on estimated rates of vapor transport.
REFERENCES


Use of Column Studies and a Reactive Transport Model to Measure Biodegradation Rates of Hydrocarbons

By Ronald J. Baker and Arthur L. Baehr

Abstract

A laboratory method for determining biodegradation rates of volatile hydrocarbons in unsaturated porous media (subsurface sedimentary material) was developed. Glass columns were filled with samples of porous media from the unsaturated zone at a gasoline-contaminated site in Galloway Township, N.J. Vapor-phase hydrocarbons (benzene, toluene, or p-xylene) were added to the porous media at the bottom of the column and were transported vertically along a concentration gradient. Aerobic biodegradation of hydrocarbons is indicated by the production of carbon dioxide ($CO_2$). The vapor-phase hydrocarbon and $CO_2$ concentrations were monitored at several depths through sampling ports. Fluxes of hydrocarbons and $CO_2$ leaving the column also were measured frequently. A mathematical model was used to calculate $CO_2$-production rates as a function of depth. These distributions and stoichiometric relations describing hydrocarbon biodegradation were used to calculate depth-specific hydrocarbon-degradation rates. Degradation rates generally increased with depth, and appeared to be coupled to soil-moisture content, which also increased with depth. Degradation rates also increased with the number of methyl groups on the aromatic ring, and rates were greater in unprocessed sediment than in sieved sand from which fine particles had been removed. This method could be used to determine optimum bioremediation conditions in the design of bioremediation strategies.

INTRODUCTION

An estimated 75,000 to 100,000 underground gasoline- and other fuel-storage tanks in the United States currently are leaking (Brown and others, 1985), causing widespread contamination of ground water by benzene, toluene, xylenes, ethylbenzene, and other toxic hydrocarbon components. The fact that hydrocarbons from petroleum products are degraded in the subsurface by indigenous microbes has been established (Atlas, 1984). Biodegradation rates must be quantified to assess the importance of this process as an attenuating mechanism under conditions associated with either in situ bioremediation or no-action scenarios.

Rates of biodegradation can be estimated by monitoring vapor-phase geochemical signatures of hydrocarbon biodegradation (for example, concentration gradients and fluxes of oxygen ($O_2$), $CO_2$, and hydrocarbons). These gas constituents have been monitored extensively during ongoing research at the site of a crude-oil spill in Bemidji, Minn. (Baedecker and others, 1989), and at a gasoline-spill site in Galloway Township, N.J. (Baehr and Fischer, 1996).

One component of the research at the Galloway Township site is the determination of hydrocarbon-biodegradation rates in laboratory columns filled with samples of unsaturated porous media collected at the site. The columns are designed to maintain constant conditions over long periods of time (months), and to provide conditions that more closely approximate natural geochemical conditions than a closed-microcosm approach does. When the columns are aligned vertically, a stable moisture gradient forms that is representative of the moisture gradient typically observed in the unsaturated zone above the capillary zone. A stable gradient of vapor-phase hydrocarbon concentration also forms. This gradient is representative of conditions in the field, where contaminant concentrations typically decrease with distance from the contaminant source.
Aromatic hydrocarbons readily biodegrade under aerobic conditions (Atlas, 1984), resulting in consumption of O₂ and production of CO₂ and biomass. Molar ratios of O₂ consumption, hydrocarbon consumption, and CO₂ production can be derived stoichiometrically from relevant reactions. For example, representative reactions for toluene biodegradation are as follows:

- **Mineralization of hydrocarbons to CO₂:**
  \[ \text{C}_7\text{H}_8 + 9 \text{O}_2 \rightarrow 7 \text{CO}_2 + 4 \text{H}_2\text{O} \]  
  Molar ratios: 1.00 toluene : 9.00 O₂ : 7.00 CO₂

- **Conversion of hydrocarbons to biomass:**
  
  \[ 7\text{C}_7\text{H}_8 + 9\text{H}^+ + 9\text{NO}_3^- \rightarrow 9\text{C}_5\text{H}_7\text{O}_2\text{N} + 4\text{CO}_2 + 1\text{H}_2\text{O} \]  
  Molar ratios: 1.00 toluene : 1.28 NO₃ : 0.57 CO₂

- **Endogenous respiration of biomass to CO₂:**
  \[ \text{C}_5\text{H}_7\text{O}_2\text{N} + 5\text{O}_2 + \text{H}^+ \rightarrow 5\text{CO}_2 + \text{NH}_4^+ + 2\text{H}_2\text{O} \]  
  Molar ratios: 1.00 Biomass : 5.00 O₂ : 5.00 CO₂ : 1.00 NH₄⁺

Stoichiometric ratios allow for calculation of reaction rates for one chemical constituent in terms of another. This approach was used in this work, where hydrocarbon-utilization rates were not directly measurable, but were calculable from CO₂ production rates.

This paper describes the development of the column apparatus used to (1) determine biodegradation rates, (2) measure biodegradation rates of hydrocarbons in columns of unsaturated porous media from the Galloway Township site, and (3) determine depth-specific hydrocarbon-biodegradation rates by use of a mathematical model.

**EXPERIMENTAL METHOD AND MATERIALS**

The experimental column design is shown in figure 1. Five 10-cm internal diameter glass columns each have six ports for vapor-phase sampling. A stainless-steel screen near the bottom of the column supports the porous media. The bottom reservoir provides a constant source of hydrocarbons, which evaporate and diffuse upward through the column. In the experiments reported here, pure liquid aromatic hydrocarbons were placed in the bottom reservoir. A gas-filled chamber above the porous media was purged continuously with a mixture of compressed gases referred to as the sweep-gas. The sweep-gas composition can be varied to produce desired experimental conditions (for example, air for aerobic conditions and nitrogen for anaerobic experiments). A hydrocarbon-concentration gradient defined by high hydrocarbon concentration near the reservoir source and low concentration near the sweep gas was established. The composition of the gaseous phase of the porous media was determined by analyzing samples collected by syringe from the ports by using gas chromatography. Details of the methods are presented in Baker (1993).

Sediment samples were collected from the Galloway Township site with a hand auger. A white sand layer was sampled from the depth of the perched water table, about 3.5 m below land surface near the location vapor sampling well VW-9 (Fischer and others, 1996). This location is near the center of the hydrocarbon contaminant plume and also is a zone of active microbial degradation. Either the sand was directly placed in the glass columns (in the unprocessed-sediment experiment) or a fraction was prepared by sieving the sand and filling the columns with the predominant grain-size range of 0.25 to 1.0 mm (in the sieved-sand experiments). Sieved sand was prepared further by washing to remove fines and oven-drying at about 150 °C. The sieved sand was mixed with a small amount (2 percent) of unprocessed sediment from the area of vapor well VW-9 to inoculate it with microorganisms from the Galloway Township site. Additional inoculation was accomplished by flooding the porous media with hydrocarbon-contaminated ground water taken from VW-9, then draining by gravity.
MATHEMATICAL MODELING

Mathematical modeling is required to determine the reaction rates for reactive vapor-phase chemical constituents (hydrocarbon, O₂, and CO₂) as a function of column depth (R_k(Z)) and, therefore, as a function of gaseous-phase composition and moisture content, which vary with column depth. Reaction rates are determined by calibration of the model to experimental data. The model expands on the work of Baehr and Bruell (1990) to include reactive-transport quantification. The modeling approach is outlined here, and is presented in greater detail by Baker (1993).

If the time scale over which changes in reaction rates occur is long compared to the time scale defining the physical redistribution of gases, then it is appropriate to analyze the data from each synoptic sampling (sampling and analysis of the vapor-phase composition, requiring 2-3 days) with a steady-state model. Therefore, for each modeling application the reaction rates (R_k(Z)) can vary along the length of the column, and are fixed in time if a steady-state gas distribution is assumed. The long-term time dependence of the reaction rates can be defined by reapplying the steady-state model to the results of a subsequent synoptic sampling and redefining the reaction rates. This approach is defined as a quasi-steady-state approach—that is, the transient experimental behavior is approximated by a finite number of steady-state “snapshots.”

The model is based on conservation-of-mass equations describing the transport and reaction of individual constituents of a multicomponent gas. For each constituent, the following equation applies:

\[ \frac{dJ_k}{dz} = R_k(z) \quad k = 1,2,\ldots, M \quad (4) \]

where \( z \) is the distance in centimeters from the top of the porous media to a depth being considered in the column; \( J_k \) is the mass flux, in grams per square centimeter per second for the \( k \)th constituent; \( R_k(z) \) is the rate of production or consumption (reaction rate) of the \( k \)th constituent, in grams per cubic centimeter per second; and \( M \) is the number of constituents. Although the porous media may contain an aqueous phase, experimental conditions are such that the aqueous phase is stationary and is assumed to be in chemical equilibrium with the gaseous-phase. The fluxes, \( J_k \), are defined by transport properties of the porous media, gaseous-phase concentration gradients, and boundary conditions

defined at the sweep-gas location. A key parameter used in the model is tortuosity (\( \tau \)), which relates bulk diffusion coefficients to the effective diffusion coefficients of gas-phase constituents in the porous media as follows

\[ D_k = D^b_k \theta_a \tau \quad (5) \]

where \( D_k \) is the effective diffusion constant of \( k \) in the porous media, \( D^b_k \) is the bulk vapor-phase diffusion constant of \( k \), \( \theta_a \) is the gas-filled porosity, and \( \tau \) is the tortuosity.

Although tortuosity can not be measured directly, it can be obtained by using a parameter-fitting technique included in the model in which concentration-gradient data and flux data for a gas-phase constituent are fitted to a depth-dependent distribution of tortuosity values. Any gas-phase constituent with a concentration profile that is not measurably affected by microbial degradation can be used in this calibration.

BIODEGRADATION RATES

Total rates of CO₂ production and hydrocarbon biodegradation for each of the five experiments are shown in table 1. Sweep-gas CO₂ concentration and sweep-gas flow rate were used to obtain the total CO₂ flux for each column which, at steady state, is equal to total CO₂ production in the column. Hydrocarbon-degradation rates were calculated from CO₂-production rates by using stoichiometric relations, such as the one in equation 1.

For the three aromatic hydrocarbons studied, degradation rates increased as the number of methyl groups increased. Toluene degradation was more rapid in unprocessed sediment than in sieved sand, probably as the result of the presence of fine particles in the unprocessed sediment, which provided increased surface area and a more complete inorganic nutrient mixture for microbial activity.

Uniform hydrocarbon-degradation rates cannot be assumed over the length of a column because the columns are heterogeneous with respect to vertical moisture distribution and hydrocarbon concentration. Therefore, the degradation rates listed in table 1 are mass-averaged over the entire column, and depth-specific degradation rates (R_k(z)) are determined by application of the mathematical model.
Table 1. Total hydrocarbon biodegradation, experiments A-E

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Compound</th>
<th>Porous media dry mass (g)</th>
<th>Pore water volume (mL)</th>
<th>CO₂ produced (mg/d)</th>
<th>Hydrocarbon degraded (mg/d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A sieved</td>
<td>Benzene</td>
<td>6,653</td>
<td>163.4</td>
<td>3.7</td>
<td>1.1</td>
</tr>
<tr>
<td>B sieved</td>
<td>Toluene</td>
<td>6,681</td>
<td>217.7</td>
<td>5.3</td>
<td>1.6</td>
</tr>
<tr>
<td>C sieved</td>
<td>p-Xylene</td>
<td>6,699</td>
<td>229.2</td>
<td>16.6</td>
<td>4.9</td>
</tr>
<tr>
<td>D sieved*</td>
<td>Toluene</td>
<td>6,663</td>
<td>309.7</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>E unprocessed</td>
<td>Toluene</td>
<td>7,124</td>
<td>263.9</td>
<td>27.7</td>
<td>8.2</td>
</tr>
</tbody>
</table>

* sterile control

Tortuosity was determined as a function of column depth ($t(z)$) through model calibration, and is plotted for Experiment A (sieved sand, benzene) in figure 2. Tortuosity near the lower boundary of the column was observed to be generally lower than tortuosity near the top of the column. This observation was anticipated because moisture content was higher at the bottoms of the columns than at the tops.

Depth-dependent CO₂-production rates were determined by using the mathematical model; these rates were converted to hydrocarbon-degradation rates with the assumption of complete mineralization. Figure 3 shows benzene degradation as a function of column depth for Experiment A (sieved sand, benzene). Biodegradation rates were highest near the bottoms of the columns, where moisture levels were highest, yet less than saturation. Biodegradation rates are expected to increase with moisture levels because the microbial community resides in the aqueous film adhering to the porous media, and because hydrocarbons are available for biodegradation only in dissolved form; therefore, the available mass of hydrocarbon substrate is proportional to the moisture content.

**SUMMARY**

A laboratory column experiment method in conjunction with a mathematical model was applied successfully to quantify hydrocarbon-biodegradation rates as a function of depth-dependent parameters (hydrocarbon concentration and moisture content) in unsaturated porous media. Under the experimental conditions presented, CO₂ flux was used as an indicator of hydrocarbon-degradation rates because the hydrocarbon and oxygen gaseous-phase concentration profiles
were not measurably affected by the microbial activity. This method could be used to determine optimum conditions for hydrocarbon biodegradation in the design of bioremediation strategies. Moisture, nutrient, and organic-compound substrate concentrations as well as temperature are variables that could be considered in the column-study design.

REFERENCES CITED


Method for Monitoring Biodegradation of Hydrocarbons in Unsaturated Porous Media

By John G. Nolan¹, Ronald J. Baker², and Arthur L. Baehr²

Abstract

A method for monitoring reaction rates of reactants and products during biodegradation of hydrocarbons in unsaturated porous media was developed. Stainless-steel bioreactors were filled with porous media that had been collected from a gasoline-spill site and used in biodegradation column studies. The purpose of the bioreactor study was to test the hypothesis that the microbial population in the porous media taken from the columns was at steady-state with respect to biomass production and endogenous respiration. This hypothesis allows hydrocarbon-biodegradation rates to be calculated from carbon dioxide production rates or oxygen consumption rates if mineralization stoichiometry is assumed. Toluene and p-xylene were the hydrocarbons used.

INTRODUCTION

Gasoline spills cause widespread subsurface-contamination problems in the United States. Remediation of gasoline-spill sites can be achieved by natural or enhanced biodegradation of gasoline hydrocarbons. Rates of microbial degradation of hydrocarbons are needed to estimate the rate of bioremediation. In situ biodegradation rates can be inferred from results of microcosm experiments (Aamond and others, 1989) conducted with aqueous and solid samples collected from a contaminated site.

Typically, a microcosm experiment is conducted in a closed system. Because concentrations of biodegradable contaminants begin to decrease as soon as the microcosm is sealed, constant substrate concentrations and microbial populations are rarely achieved. In contrast, field conditions are open systems, in which quasi-steady-state conditions with relatively stable microbial populations and hydrocarbon substrate concentrations would be expected. Therefore, kinetic information derived from microcosm experiments may not accurately reflect in situ biodegradation rates.

An alternative approach to estimating biodegradation rates in which conditions of hydrocarbon and oxygen (O₂) concentrations and microbial populations are maintained in open columns of porous media is presented by Baker and Baehr (1996). In this approach, the hydrocarbon substrate is present in excess, and its utilization rate is not directly measurable. Therefore, stoichiometric relations describing hydrocarbon biodegradation are used to calculate hydrocarbon reaction rates from measured carbon dioxide (CO₂) production rates or from O₂ consumption rates. In order to verify the validity of such stoichiometric conversions, a means of determining complete mass balances of the principal bioreactive chemical constituents in known quantities of porous media is needed. Such a method was developed and verified in this study. The hypothesis was that mineralization (complete conversion to CO₂ and water) is the dominant fate of the hydrocarbons in the columns, and that calculating hydrocarbon biodegradation from CO₂ production or O₂ consumption is appropriate. A stainless-steel bioreactor and a set of experiments were designed for testing this hypothesis. The objective of this study was to determine whether the microbial population in the porous media is at steady-state with respect to biomass production and endogenous respiration. This paper summarizes the experiments conducted to test this hypothesis. A detailed description is presented by Nolan (1993).

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Experimental Method

Samples of porous media from the column experiments of Baker and Baehr (1996) were collected and and known amounts were placed into gas-tight stainless-steel bioreactors. The bioreactors were then spiked periodically (generally at 48-hour intervals) with a fixed amount of a hydrocarbon (either toluene or p-xylene) and \( \text{O}_2 \). At the start of the experiment, known quantities of the specified hydrocarbon, \( \text{O}_2 \), and \( \text{CO}_2 \) were present in each bioreactor. Vapor samples extracted during the spiking process were analyzed by gas chromatography to quantify the mass of hydrocarbons, \( \text{O}_2 \), and \( \text{CO}_2 \) present in the bioreactors at the time of sampling. Because all major bioreactive species were monitored, the reaction rates of the hydrocarbon, \( \text{O}_2 \), and \( \text{CO}_2 \) could be determined at any time. Therefore, steady-state and mineralization assumptions could be tested.

The bioreactors consisted of 12-in.-long, 1/2-in. I.D. Schedule 40 stainless-steel pipes with threaded stainless-steel endcaps. The endcaps were fitted with three vapor-sampling ports formed from three 1/16-in. threaded holes cut into each bioreactor--two near the endcaps and one at the center. The port assembly included a threaded fitting sealed with a Viton O-ring (1/8 in.) and capped with a compression fitting (1/16 in.) and an 18-gauge stainless-steel syringe needle. The needle was capped with a syringe valve.

Unsaturated porous media for the experiments were taken from two columns in which unprocessed sediment from a gasoline-spill site in Galloway Township, N.J., had been exposed to aromatic hydrocarbons for a period exceeding 1 year (Baker and Baehr, 1996). One column experiment was conducted with toluene, the other with p-xylene. The porous media placed in each bioreactor were microbially acclimated to the hydrocarbon selected. Approximately 350 cm\(^3\) of sediment was packed into each bioreactor.

Materials (porous media) were taken from the toluene- and p-xylene-amended glass columns, and seven cylinder bioreactors were established and labeled as indicated in table 1. The sterile control bioreactors designated TC and XC were filled with a mixture of material from all three zones of the glass column, autoclaved for 2 hours at 120 °C, and dosed with silver nitrate (200-mg/L solution).

The bioreactors were spiked with \( \text{CO}_2 \)-free air (about 79 percent nitrogen and 21 percent \( \text{O}_2 \) by volume) containing known amounts of toluene or p-xylene. Every 48 hours a sample was collected from the bioreactor while an equal volume of hydrocarbon/air mixture was injected. The sample was analyzed by gas chromatography as described in Baker (1993) to determine the hydrocarbon, \( \text{O}_2 \), and \( \text{CO}_2 \) concentrations. A mass balance of these constituents was maintained throughout each experiment.

In order to maintain a mass balance, the quantities of hydrocarbons, \( \text{O}_2 \), and \( \text{CO}_2 \) partitioned among the gaseous and aqueous phases in the bioreactors had to be considered. The solid phase was not considered because the sediment was not found to adsorb significant amounts of hydrocarbons, and would not be expected to retain \( \text{O}_2 \) or \( \text{CO}_2 \). Aqueous-phase \( \text{CO}_2 \) and \( \text{O}_2 \) concentrations were calculated from vapor-phase concentrations if Henry's law is assumed. The cumulative number of millimoles of constituents consumed or produced in the reactor was monitored through time. Counts of total viable microorganisms were carried out at the beginning and end of each experiment.

### Table 1. Porous media used in bioreactors

<table>
<thead>
<tr>
<th>Compound</th>
<th>Label</th>
<th>Location of material within glass column</th>
<th>Water-filled porosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>T1</td>
<td>Unsaturated zone</td>
<td>0.0581</td>
</tr>
<tr>
<td></td>
<td>T2</td>
<td>Water-table zone</td>
<td>0.1372</td>
</tr>
<tr>
<td></td>
<td>T3</td>
<td>Saturated zone</td>
<td>0.2313</td>
</tr>
<tr>
<td>TC (control)</td>
<td></td>
<td>Mixture from all zones</td>
<td>0.1533</td>
</tr>
<tr>
<td>p-Xylene</td>
<td>X1</td>
<td>Unsaturated zone</td>
<td>0.1010</td>
</tr>
<tr>
<td></td>
<td>X2</td>
<td>Water-table zone</td>
<td>0.1119</td>
</tr>
<tr>
<td>XC (control)</td>
<td></td>
<td>Mixture from all zones</td>
<td>0.1375</td>
</tr>
</tbody>
</table>

### BIODEGRADATION OF HYDROCARBONS

Hydrocarbon degradation and \( \text{CO}_2 \) production in sterile control bioreactors TC and XC were negligible. Therefore, all hydrocarbon consumption and \( \text{CO}_2 \) production in the live reactors T1 through T3 and X1 through X2 was attributed to microbial activity.

Table 2 shows cumulative millimoles of toluene degradation, \( \text{CO}_2 \) production, and \( \text{O}_2 \) consumption over time for experiments T1-T3. If mineralization is the dominant fate of the hydrocarbons, then the rates of change in the constituents are related according to the mineralization equation for toluene as follows:

\[
1 \text{ C}_7\text{H}_8 + 9 \text{ O}_2 \rightarrow 7 \text{ CO}_2 + 4 \text{ H}_2\text{O}
\]

For toluene mineralization, the relative reaction rates of reactants and products on a molar basis are 1:9:7 for toluene, \( \text{O}_2 \) and \( \text{CO}_2 \), respectively.
Table 2. Results of experiments T1 through T3—Reactant and product reaction-rate data
[Values in cumulative millimoles]

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Time (days)</th>
<th>Toluene degraded</th>
<th>Oxygen consumed</th>
<th>Carbon dioxide produced</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1</td>
<td>2.05</td>
<td>0.0295</td>
<td>0.4334</td>
<td>0.2127</td>
</tr>
<tr>
<td>T1</td>
<td>5.97</td>
<td>0.0763</td>
<td>1.0851</td>
<td>0.5058</td>
</tr>
<tr>
<td>T1</td>
<td>13.95</td>
<td>0.1452</td>
<td>2.0599</td>
<td>1.6472</td>
</tr>
<tr>
<td>T1</td>
<td>27.97</td>
<td>0.2712</td>
<td>3.6453</td>
<td>2.9848</td>
</tr>
<tr>
<td>T2</td>
<td>2.03</td>
<td>0.0184</td>
<td>0.1370</td>
<td>0.0890</td>
</tr>
<tr>
<td>T2</td>
<td>5.97</td>
<td>0.0542</td>
<td>0.3825</td>
<td>0.2723</td>
</tr>
<tr>
<td>T2</td>
<td>13.95</td>
<td>0.1216</td>
<td>0.6863</td>
<td>0.5894</td>
</tr>
<tr>
<td>T2</td>
<td>27.97</td>
<td>0.2385</td>
<td>1.1832</td>
<td>1.0460</td>
</tr>
<tr>
<td>T3</td>
<td>2.03</td>
<td>0.0178</td>
<td>0.0024</td>
<td>0.1347</td>
</tr>
<tr>
<td>T3</td>
<td>6.01</td>
<td>0.0539</td>
<td>0.3730</td>
<td>0.3414</td>
</tr>
<tr>
<td>T3</td>
<td>13.96</td>
<td>0.1253</td>
<td>0.6708</td>
<td>0.8236</td>
</tr>
<tr>
<td>T3</td>
<td>27.97</td>
<td>0.2437</td>
<td>1.2379</td>
<td>1.2883</td>
</tr>
</tbody>
</table>

Normalized concentration data are shown in figures 1-3. The amount of each constituent degraded, produced, or consumed (from Table 2) is divided by its corresponding stoichiometric coefficient from the mineralization equation. If the three lines showing rates of toluene degradation, O2 consumption, and CO2 production as a function of time coincide, complete mineralization is indicated. If the slope of the hydrocarbon degradation line is less than those of the O2 consumption and CO2 production lines, then more O2 is being utilized and more CO2 is being produced than is accounted for by the degradation of the hydrocarbon. This observation indicates that there is net endogenous decay of microorganisms, and that the system is not in steady-state with respect to biomass. This condition was noted for T1 during the first 28 days of the experiment. When the slope of the hydrocarbon degradation

Figure 1. Stoichiometrically normalized cumulative toluene degradation, oxygen consumption, and carbon dioxide production as a function of time—results of experiment T1 (toluene, unsaturated zone).
Figure 2. Stoichiometrically normalized cumulative toluene degradation, oxygen consumption, and carbon dioxide production as a function of time—results of experiment T2 (toluene, water-table zone).

These data indicate that microbial populations were adjusting to the bioreactor environment during the experiment, either decreasing (T1) or increasing (T2, T3, X2). Two questions need to be addressed for the application of the method: (1) is the bioreactor environment significantly different from the column environment, and could this difference lead to microbial-population changes, and (2) should mineralization stoichiometry be abandoned. The answer to the first question is that the saturated-unsaturated column environment was significantly different from that of the unsaturated bioreactors: hydrocarbon loading rates also were different. Therefore, adjustment of the microbial population would be expected. For the p-xylene-amended bioreactors, counts of total viable microorganisms at the beginning and end of the exper-
Figure 3. Stoichiometrically normalized cumulative toluene degradation, oxygen consumption, and carbon dioxide production as a function of time—results of experiment T3 (toluene, saturated zone).

Table 3. Measured and Calculated Hydrocarbon Degradation Rates

<table>
<thead>
<tr>
<th>Day</th>
<th>Experiment</th>
<th>Millimoles of hydrocarbon consumed (measured)</th>
<th>Calculated millimoles of hydrocarbon consumed</th>
<th>Percent error</th>
<th>Percent error</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>T1</td>
<td>0.2353</td>
<td>0.1452</td>
<td>+62.0</td>
<td>+57.6</td>
</tr>
<tr>
<td>14</td>
<td>T2</td>
<td>0.0842</td>
<td>0.1216</td>
<td>-30.7</td>
<td>-37.3</td>
</tr>
<tr>
<td>14</td>
<td>T3</td>
<td>0.1177</td>
<td>0.1253</td>
<td>-6.1</td>
<td>-40.5</td>
</tr>
<tr>
<td>28</td>
<td>T1</td>
<td>0.4264</td>
<td>0.2712</td>
<td>+57.2</td>
<td>+49.3</td>
</tr>
<tr>
<td>28</td>
<td>T2</td>
<td>0.1494</td>
<td>0.2385</td>
<td>-37.3</td>
<td>-44.9</td>
</tr>
<tr>
<td>28</td>
<td>T3</td>
<td>0.1840</td>
<td>0.2437</td>
<td>-24.5</td>
<td>-43.6</td>
</tr>
<tr>
<td>36</td>
<td>X1</td>
<td>0.3765</td>
<td>0.3868</td>
<td>-2.7</td>
<td>+10.3</td>
</tr>
<tr>
<td>22</td>
<td>X2</td>
<td>0.0442</td>
<td>0.0900</td>
<td>-50.9</td>
<td>-48.9</td>
</tr>
<tr>
<td>72</td>
<td>X1</td>
<td>0.6497</td>
<td>0.6916</td>
<td>-6.0</td>
<td>+1.0</td>
</tr>
<tr>
<td>46</td>
<td>X2</td>
<td>0.1013</td>
<td>0.1904</td>
<td>-46.8</td>
<td>-35.3</td>
</tr>
</tbody>
</table>
Sediments are evidence of an adjustment in total viable count. The X1 viable count remained relatively constant, decreasing slightly from $3.3 \times 10^7$ to $2.3 \times 10^7$ viable cells per gram of sediment. This observation is consistent with the vapor-analysis reaction data, which closely follow the mineralization ratios of reactants and products. The X2 viable microbial count, however, increased from $3.3 \times 10^3$ to $4.9 \times 10^4$ viable cells per gram of sediment, resulting in a loss of CO$_2$ mass associated with biomass production. This phenomenon is consistent with the observed high rate of p-xylene utilization relative to the observed rate of CO$_2$ production. The errors associated with calculating hydrocarbon-degradation rates from CO$_2$ production are significant; however, in the most extreme case, the rate of hydrocarbon degradation would be overestimated or underestimated by 50 percent on the basis of CO$_2$ production. Therefore, the mineralization stoichiometry is valid.

CONCLUSIONS

A mass-balance approach to testing assumptions of biomass steady-state and hydrocarbon mineralization in porous media was developed. The stainless-steel bioreactors enabled long-term monitoring of bio-reactive species in porous media while hydrocarbon and oxygen were added to the system periodically to approximate open-system conditions. The vapor-analysis-concentration data indicate that the mineralization hypothesis provides a reasonable stoichiometry for computing hydrocarbon-degradation rates from inorganic-gas-concentration data. Suggested improvements to the experimental method include extension of the period of the experiment in order to track the transition to a mineralization-dominated process completely, while providing a more continuous (less incremental) way of introducing hydrocarbons and O$_2$ to the system. This could be achieved by increasing reactor size and sampling frequency and decreasing sample volume. Conditions can be maintained purposely to observe stoichiometry under conditions favoring biosynthesis (sparingly inoculated sediment) or decay (starvation conditions). Finally, radioactive tracers could be used to improve the accuracy of carbon mass-balance calculations.

REFERENCES


Optimizing the Design of Vapor-Extraction Remediation Systems for Removal of Organic Contaminants From the Unsaturated Zone

By Claire Welty¹, Craig J. Joss², and Arthur L. Baehr³

Abstract

A new mathematical model has been developed that can be used in the design of vapor-extraction and bioventing systems for removing organic contaminants from the unsaturated zone. The model has two major components: a three-dimensional finite-difference model of air flow in unsaturated porous media (AIR3D), and an algorithm that couples the three-dimensional air-flow model with mathematical programming (OPTAIR).

AIR3D is based on the flow of an ideal gas in porous media. The code consists of a preprocessor and postprocessor to be used with the U.S. Geological Survey ground-water flow simulator MODFLOW to solve the conservation-of-mass equation for air flow in a discretized three-dimensional domain. OPTAIR couples AIR3D with an optimization algorithm, to allow a user to determine the optimal number and arrangement of well screens and rates of air withdrawal or injection in the domain to obtain the most efficient design.

INTRODUCTION

In situ vapor extraction has become a widely used technique for remediating unsaturated zones contaminated with volatile chemicals. Figure 1 is a schematic of the process. Forcing air through the unsaturated zone also is recognized as a means of enhancing aerobic biodegradation of hydrocarbons. A method of predicting and quantifying both the flow paths of forced air in the unsaturated zone and the radius of influence resulting from air withdrawal or injection is needed for designing such vapor-extraction and bioventing systems. In addition, a method for determining the optimal number and arrangement of well screens and rates of air withdrawal and injection in the domain is desirable for optimizing cleanup efficiency. Two modeling tools have been developed for use in designing these systems for a given site: a three-dimensional numerical model of air flow through porous media, and an algorithm that couples the air-flow model with mathematical programming for evaluating the optimal combination of numbers, flow rates, and placement of air withdrawal, injection, and passive wells.

At the previous U.S. Geological Survey Toxic Substances Hydrology technical meeting, held in Monterey, California, in 1991, we presented a paper outlining our approach for modeling vapor-extraction systems in the unsaturated zone (Welty and others, 1991a). This paper describes the implementation of our approach and provides references for other reports resulting from this work.

DEVELOPMENT OF A THREE-DIMENSIONAL AIR-FLOW MODEL

The three-dimensional equation for air flow is derived by combining the conservation-of-mass equation for air flow in unsaturated porous media and the Darcy equation for a compressible fluid. By assuming further that air density and pressure are

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related by the ideal-gas law (Baehr and Hult, 1991), the following field equation results:

\[
\frac{\partial}{\partial x} \left( k_{xx} \frac{\partial \phi}{\partial x} \right) + \frac{\partial}{\partial y} \left( k_{yy} \frac{\partial \phi}{\partial y} \right) + \frac{\partial}{\partial z} \left( k_{zz} \frac{\partial \phi}{\partial z} \right) = S_a \frac{\partial \phi}{\partial t} \quad (1)
\]

where \( \phi = P^2 \), with \( P \) = air-phase pressure. The substitution \( \phi = P^2 \) has been made to linearize the equation. The Cartesian coordinates have been aligned with the principal directions of anisotropy so that \( k_{xx}, k_{yy}, \) and \( k_{zz} \) are the principal components of the air-phase permeability tensor. Air-phase permeability represents the permeability available to the gas phase in unsaturated porous media. It is not equivalent to intrinsic permeability as a result of the presence of liquid phases in the pore space.

\( S_a \) in eq. 1 is an air-storage term defined as

\[
S_a = \frac{\theta \mu}{\phi^{1/2}}. \quad (2)
\]

where \( \theta \) is the air-filled porosity (assumed to be constant with respect to time) and \( \mu \) is the dynamic viscosity of air. Equation 1 is linearized by assuming that \( \phi^{1/2} \) in equation 2 is the (constant) prevailing atmospheric pressure. Equation 1 is derived by assuming that the Klinkenberg slip effect, the temperature gradient, and the elevation component of pneumatic head are negligible; the average molecular weight of air and air-filled porosity are constant; and the Darcy equation and the ideal-gas law apply. Baehr and Hult (1991) evaluated the consequences of these assumptions and showed that the linear air-flow model given by eq. 1 is a good working model for vapor extraction and many other environmental applications.

The three-dimensional field equation for saturated ground-water flow is identical in mathematical form to eq. 1 when the following substitutions are made:

\[
h \Rightarrow \phi \quad (3a)
\]

\[
K_{ii} \Rightarrow k_{ii} \quad (i=x,y,z) \quad (3b)
\]

\[
S_s \Rightarrow S_a. \quad (3c)
\]

where \( h \) is potentiometric head; \( K_{xx}, K_{yy}, \) and \( K_{zz} \) are saturated hydraulic conductivities in the three principal directions of anisotropy; and \( S_s \) is specific storage. This mathematical equivalency can be used to advantage to solve eq. 1, because many well-documented, widely used computer codes have been published to solve the ground-water flow equation. We have taken the approach of using the ground-water-flow code MODFLOW (McDonald and Harbaugh, 1988) to solve eq. 1.

The air-flow model AIR3D consists of three components. First, a preprocessor (PREAIR) converts a pneumatic problem to a hydraulic-equivalent one.
Next, the hydraulic-equivalent problem is solved by using MODFLOW. For the last step, a postprocessor (POSTAIR) converts the hydraulic output to pneumatic units. PREAIR and POSTAIR are written in Fortran 77, and can be used on any computer with an installed Fortran 77 compiler. We have run these codes on PRIME 6350 and IBM 9121 mainframes, and on IBM and Macintosh personal computers. The three codes PREAIR, MODFLOW, and POSTAIR comprise the solution to eq. 1, which we have named AIR3D (Joss and Baehr, 1994).

In AIR3D, we model a well by specifying constant pressure along the well-screen length. (This approach also could be adapted for ground-water-flow modeling in place of specifying a uniformly distributed discharge over the length of a well screen.) This naturally simulates the variation in flow rate along the length of the well screen that occurs when a well passes through layers of varying air permeability. A disadvantage of this approach is that the volumetric and mass flow rates at the well corresponding to a specified pressure condition are not known until after a simulation is completed. If a particular volumetric or mass flow rate is desired, simulations must be performed iteratively to determine the well pressure that must be specified to yield the desired average flow rate. This procedure could be tedious for simulations involving multiple wells. The solution to this iterative problem is a default application of the optimization procedure discussed in the next section. In addition to the well-screen delineation, other boundary conditions can be specified to match a given application. For example, a macadam surface of limited areal extent can be part of the upper boundary, while the water table is fixed as a no-flow lower boundary.

Because vapor cleanup is proportional to calculated air-flow rates, modeling is an inexpensive alternative to field pilot testing. The accuracy of model predictions depends, however, on the availability of air-phase permeability data, which are site-specific. Joss and others (1992), and Baehr and Hult (1991) describe field techniques for evaluating unsaturated-zone air permeability. Baehr and Hult (1991) derived two-dimensional, axisymmetric analytical models for air flow to a single well in an unsaturated, homogeneous, anisotropic porous medium that can be used to solve the inverse air-flow problem (finding air-phase permeability from data obtained during a pneumatic test of the unsaturated zone). These analytic models have been used in the field application cited above and are implemented as the Fortran 77 code AIR2D (J.C. Joss and A.L. Baehr, U.S. Geological Survey, written commun., 1993).

USE OF SIMULATION COUPLED WITH OPTIMIZATION OF THREE-DIMENSIONAL AIR FLOW

Although it is possible to find an efficient design for a vapor-extraction system by carrying out a number of simulations with various combinations of well-screen locations and air-injection/withdrawal rates, the most efficient design may not be found by using such a trial-and-error procedure. Many possible combinations of design parameters exist and identification of a best set of choices for test simulations may not be readily apparent for heterogeneous soils and complex site-boundary conditions. A more advanced level of design technology that builds on the numerical-simulation approach is formal optimization of the design variables, in which the best combination of number of wells, air-injection/withdrawal rates, and well locations is found by means of mathematical-programming (optimization) techniques commonly used in the field of operations research. A similar approach has been taken for two-dimensional aquifer management (Lefkoff and Gorelick, 1987). To optimize the design process, mathematical-programming algorithms can be coupled with AIR3D to determine the optimal set of design parameters for achieving stated venting objectives at a given site (Welty and others, 1991a and 1991b). We have implemented this coupled model as the Fortran 77 code OPTAIR (Welty and others, 1992). Typical objective functions that may be specified by a user include minimizing total costs, minimizing total-flow rates, or maximizing the flow of air over a subdomain.

OPTAIR consists of five modules, as illustrated by figure 2: PREAIR (from AIR3D), OPTAIR1, MODFLOW, any standard optimization solver, and OPTAIR2. The physical conditions characterizing a site, including distribution of air-phase permeabilities, boundary conditions, and a chosen finite-difference grid, are specified as inputs to PREAIR. PREAIR is invoked to generate the hydraulic equivalent of the pneumatic problem written as MODFLOW input files. Trial well-screen locations, any physical or economic constraints, objective-function coefficients, and decision variables are specified as inputs to OPTAIR1. For every trial well-screen location, OPTAIR1 calls MODFLOW to evaluate the response of the physical system to the specified well-screen condition, and uses
the response-matrix method (Lee and Aronofsky, 1958) to generate an optimization-problem formulation in standard mathematical-programming system (MPS) format. The current version of OPTAIR can generate any linear-programming problem; future versions will include mixed-integer/linear capabilities as outlined by Welty and others (1992), so that the fixed costs associated with well-screen installation can be included in specifying a cost-minimization problem.

Any optimization algorithm that reads MPS-formatted input can be invoked to solve the linear-programming problem as written by OPTAIR1. We used LINDO (Schrage, 1991) on mainframes and personal computers. The output from the optimization algorithm specifies optimal flow rates at all trial well-screen locations. An optimal flow rate of zero means that the trial well location should not be chosen as part of the final solution. The output from the optimization software is given in terms of the hydraulic-equivalent problem, however, and must be converted to pneumatic units. This calculation is carried out by OPTAIR2. An independent check by the user is needed to determine whether the recommended flow-pressure relations at stress points are physically obtainable—that is, fall within a pump’s capacity as defined by a rating curve.

**INCORPORATION OF VAPOR-TRANSPORT FEATURES IN FUTURE RESEARCH**

Joss (1993) developed a vapor-transport model to simulate chemical transport and degradation associated with vapor-extraction and bioventing systems. This model uses AIR3D to define the air-flow field and allows estimation of transport of multiple constituents in the gas phase, including effects of partitioning into aqueous and solid phases,
chemical reactions, and biological degradation. As proposed by Welty and others (1991a), the vapor-transport model also can be coupled with optimization algorithms to include the effects of time-dependent, decreasing vapor-constituent concentrations on design of the optimal venting-well system. This would allow incorporation of the economics of off-gas treatment in designing an optimal system, because treatment costs depend on sizing of units which, in turn, depend on the time history of cleanup. In addition, the effects of a time-variable pumping schedule on the design of an optimal remediation system could be examined.

**SUMMARY**

This paper describes two numerical models we have developed for use in vapor-extraction-system design: AIR3D, a three-dimensional finite-difference model for simulating air flow in unsaturated porous media; and OPTAIR, a coupled simulation-optimization model that can be used to determine optimal pumping rates and well-screen locations in a three-dimensional unsaturated domain. AIR2D, based on an analytical solution, can be applied to data obtained during a pneumatic test of the unsaturated zone to determine *in situ* air-phase permeabilities. Extensions of this work to include chemical-transport considerations have been described. Making these codes available in the public domain will ensure maximum availability to geologists and engineers designing vapor-extraction and bioventing systems.

**REFERENCES**


A Multispecies Transport Model to Simulate Vapor Extraction and Bioventing Remediation of Unsaturated Zones Contaminated with Gasoline

By C.J. Joss and A.L. Baehr

Abstract

Vapor extraction is an established method for removing spilled gasoline from the unsaturated zone. The technology involves the establishment of an unsaturated zone air-flow field by withdrawing and injecting air through dry well sand trenches. The success of a vapor-extraction installation depends fundamentally on the establishment of an air-flow field that intersects the contaminant and on the partitioning of the contaminant into the gaseous phase. Bioventing is a term applied to simultaneous venting and enhanced biodegradation of a contaminant. Aerobic biodegradation is stimulated by oxygen delivered to the unsaturated zone by air injection and withdrawal. A model to predict the transport and reaction of multiple chemical species in the gaseous phase under conditions of induced air flow has been developed to simulate the performance of vapor-extraction-based remediation. The model consists of a flow module and a reactive transport module. The flow module, named AIR3D, based on an adaptation of a ground-water flow simulator, defines the three-dimensional air-velocity field within which the chemicals are transported and react. The transport module solves a coupled system of conservation-of-mass equations, one for each chemical. Advection-dominance transport is assumed, which allows the conservation-of-mass equations to be defined along streamlines. In this paper, model applications and assumptions are summarized.

INTRODUCTION

Hydrocarbon contamination of ground water resulting from gasoline spills is a serious problem throughout the world. Remedial technologies that take advantage of vapor transport include vapor extraction, bioventing, and air sparging. Vapor extraction removes hydrocarbons from the unsaturated zone by inducing the flow of air laden with volatile hydrocarbons to extraction wells and off-gas treatment systems (fig. 1). Bioventing generally refers to an auxiliary benefit achieved by vapor extraction, an increase in aerobic biodegradation of hydrocarbons in the unsaturated zone as a result of increasing oxygen recharge. Air-sparging technology effects remediation of contaminated ground water by the injection of air beneath the water table. Contaminated vapor then enters the unsaturated zone, where a vapor-extraction system can be used to collect and treat the gases.

A model to predict the advective transport and reaction of multiple chemical species in the gaseous phase under conditions of induced air flow has been developed to simulate the performance of vapor-extraction-based remediation. The model development is presented in detail by Joss (1993). The objective of this paper is to outline the model assumptions and capabilities.

MODELING METHOD

Air-flow paths can be complex as a result of the effects of sediment layering, moisture variation, multiple well locations, and boundary effects caused by surface structures and paving. Therefore, in general, a numerical simulation is required to provide a three-dimensional depiction of the induced air-flow field. The authors have developed a computer code, named AIR3D, for this purpose (Joss and Baehr...
(1995). AIR3D is used to define the velocity of the gaseous phase without considering the transport of individual constituents (for example, N₂, O₂, and CO₂). Therefore, in the modeling approach, air flow is uncoupled from transport. It is anticipated that AIR3D will be applicable for making basic vapor-extraction design decisions (for example, the number of wells and the depths of their screened intervals).

Predictions of hydrocarbon-specific recovery rates (for example, the time-dependent discharge of benzene to the atmosphere from a vapor-extraction system for remediating a gasoline-spill site) and bioventing performance require a transport model. The following system of equations (Joss, 1993) defines advection-dominated receive transport for any number of chemical species along a streamline in the induced flow field:

\[
\frac{\partial}{\partial t} \left[ a_k \Gamma_k \right] + (\nabla \cdot q) G_k + \frac{q_k}{\zeta} \frac{\partial G_k}{\partial \zeta} + R_k = 0,
\]

\[k = 1, \ldots, N_f, \ldots, N.\]

In this equation, \( k \) is the index for the \( k^{th} \) constituent of the gaseous phase; \( N_f \) is the number of gaseous-phase constituents that originate from and partition significantly into an immiscible phase (for example, the hydrocarbons of gasoline); and \( N \) is the total number of gaseous-phase constituents, where \( N > N_f \) would indicate that gases other than those originating from the immiscible phase (for example, O₂, CO₂ and N₂) are part of the simulation. The variable \( t \) is time, in seconds; \( \zeta \) denotes the length coordinate, in centimeters, along any streamline; and \( q \zeta \), in centimeters per second, is the magnitude of the gaseous phase specific discharge vector, \( q \), in the streamline direction. Streamlines are defined numerically according to an uncoupled, steady-state prediction of the induced flow field, which can be generated by AIR3D. The divergence term, \((\nabla \cdot q)\), also is evaluated numerically from the steady-state flow simulation and is non-zero because the gas phase is compressible. The variable \( \Gamma_k \) indicates either the gaseous-phase concentration of the \( k^{th} \) constituent, \( G_k \), in grams per cubic centimeter of the gaseous phase (if \( k > N_f \)) or the concentration of the \( k^{th} \) constituent in the immiscible phase, \( I_k \), in grams per cubic centimeter of the immiscible phase (if \( k \leq N_f \)). The definition of the storage coefficient \( a_k \), which is unitless, depends on the definition \( \Gamma_k \), and is based on the multiphase...
equilibrium model developed by Baehr and Corapcioglu (1987a, 1987b) and applied by Joss (1993). The reaction term, \( R_k \), in grams per cubic centimeter of the porous media per second, allows for quantification of microbial reactions or any type of chemical reaction involving transformation from one constituent to another.

The model equations are solved numerically. The spatial derivatives \( \partial G_k / \partial \zeta \) are evaluated by finite-difference approximations, given a descretization of the \( \zeta \) axis. A system of \( N \) ordinary differential equations, which defines the time-dependence of chemical concentrations at each node, results. The system of equations is solved by the modified-Euler algorithm. This solution technique does not require matrix inversions and, therefore, is very efficient. Because dispersion is neglected, the solution defined on any streamline is completely uncoupled from the solution on any other streamline. Therefore, the solution throughout the three-dimensional domain is refined simply by defining additional streamlines and repeating the algorithm. Furthermore, because equation (1) is a first-order partial differential equation, boundary conditions, in the form of specified concentrations, are required only for the upstream end of a streamline (either at land surface or at an injection well) located at \( \zeta = 0 \). The numerical algorithm is presented in detail by Joss (1993).

**SUMMARY**

The environmental industry is faced with the task of removing volatile organic chemicals from the subsurface. Remediation techniques such as vapor extraction, bioventing, and air sparging are being used; therefore, a model capable of predicting chemical fate and transport in realistic induced air-flow fields is needed to facilitate design. The model outlined in this paper was developed to satisfy the need. The model consists of a flow module and a reactive transport module. First, AIR3D is used to predict flow and pressure response in three-dimensional, heterogeneous, anisotropic, multiwell domains. Steady-state flow and pressure information from the flow simulator is transferred to the transport module through use of data files. Multispecies reactive transport is then modeled by applying the conservation-of-mass principle to each constituent of the gas phase. The assumption of advection-dominated transport results in a system of first-order partial differential equations defining the conservation-of-mass principle, which are solved along streamlines. The solution defined on any streamline is completely uncoupled from the solution on any other streamline. Therefore, the solution throughout the three-dimensional domain is refined simply by defining additional streamlines and repeating the basic algorithm. This algorithm is very efficient, allowing realistic three-dimensional simulations to be performed on personal computers.

**REFERENCES**


A Comparison of Two Analytical Techniques For Identifying and Measuring the Concentrations of Volatile Hydrocarbons in Ground Water

By Curtis S. Phinney and Isabella M. Cozzarelli

Abstract

Identification of monoaromatic hydrocarbons in ground water is commonly performed in circumstances where petrochemical contamination is suspected. Presence of certain of these species is considered indicative of petrochemical contamination. Most studies of ground-water contamination focus on the fate of benzene, ethylbenzene, toluene, and the xylenes (BTEX). However, a broad range of C₆-C₁₀ aromatic hydrocarbons can be present in ground water contaminated with petroleum products. In this study, results of a comparison of two analytical techniques for the identifying and measuring the concentrations of C₆-C₁₀ monoaromatic hydrocarbons are presented. The techniques investigated are pentane/water microextraction followed by gas chromatography/flame ionization detection (GC-FID), and purge and trap (open-loop) stripping of the sample followed by GC-Ion Trap detection (GC-ITD). Open-loop/GC-ITD allows the identification of 35 C₆-C₁₀ aromatic hydrocarbons, compared to 21 identified by pentane/GC-FID. Compared to the pentane/GC method, higher sensitivity, higher selectivity, but lower precision were observed for samples analyzed by open-loop/GC-ITD.

Hydrocarbon concentrations measured by the two techniques were generally in good agreement, within 88.6-99.7 percent for total mono-aromatics. Concentrations of some trace constituents measured by pentane/GC-FID were higher under certain circumstances. For example, difficulty in resolving benzene from interferences by the pentane/GC-FID method sometimes resulted in considerably higher benzene and BTEX concentrations compared to open-loop/GC-ITD. At a sample site where hydrocarbon concentrations were low, mean BTEX concentrations (n=10) were 661 μg/L (micrograms per liter) by pentane/GC-FID compared to 490 μg/L by open-loop/GC-ITD. At a high concentration sample site, mean BTEX concentrations (n=10) were 5,077 μg/L by pentane/GC-FID compared to 5,089 μg/L by open-loop/GC-ITD.

INTRODUCTION

Techniques describing the detection and measurement of benzene, toluene, ethylbenzene, and the xylenes (BTEX) in ground water contaminated by petroleum products are well documented. These monoaromatic hydrocarbons are of interest because of the toxicity of the compounds and their relatively high solubilities and corresponding mobilities in ground-water systems (Wilson and others 1986; Barker and others, 1987). Recent studies have shown that, in addition to BTEX compounds, a broad range of other C₆-C₁₀ aromatic hydrocarbons are present in ground water contaminated with crude oil (Eganhouse and others, 1993), landfill leachate (Forst and others, 1989), and gasoline (Baedecker and others, 1991). Information on these additional compounds is potentially useful in studying the fate of petroleum hydrocarbons in ground water. The demonstrated resistance
of certain monoaromatic hydrocarbons to degradative processes in the environment suggests their utility as indicators of petroleum contamination. These relatively stable constituents can be transported farther than the BTEX compounds and may become the most abundant compound class as they propagate through the ground water system (Eganhouse and others, 1987). Improved knowledge of the fate and transport of a wider range of C₆-C₁₀ monoaromatic species could add considerably to the understanding of the physical and biological processes controlling the fate of petroleum hydrocarbons in shallow aquifers.

This study investigated the relative merits of two analytical methods that allow quantitative determination of C₆-C₁₀ aromatic hydrocarbons in ground water. The first is a pentane/water microextraction followed by gas chromatography with flame-ionization detection (pentane/GC-FID). The second method involves purge and trap stripping of the water sample with helium followed by gas chromatography with ion-trap mass-spectrometer detection (open-loop/GC-ITD). The pentane/GC-FID method required less elaborate analytical instrumentation and provides reliable information for a wide range of low molecular weight aromatic hydrocarbons. The purge and trap technique coupled with mass spectrometric detection provided highly specific qualitative determinations and in the case of the ion trap mass spectrometer, also provides a lower quantitative method detection limit (MDL). However, this instrumentation is relatively expensive and requires a higher level of operator proficiency during the collection and subsequent reduction of sample data.

This paper presents a comparison of the specificity, sensitivity, and reproducibility of the two methods for high and low concentrations of monoaromatic hydrocarbons in ground-water samples from two well-characterized locations near a subsurface gasoline spill in Galloway Township, New Jersey (Fischer and others, 1991).

DESCRIPTION OF EXPERIMENT

Site description

The field site for this study is located in Galloway Township, N.J. This site has been under investigation by the U.S. Geological Survey and the New Jersey Department of Environmental Protection since 1987. The site is approximately 10 mi. west of Atlantic City, N.J., and overlies the Cohansy Sand of the Kirkwood-Cohansey aquifer system (Zapecza, 1989). Gasoline leaking from a single storage tank on a farm contaminated ground water at a shallow domestic well (Fischer and others, 1991). Two well-characterized sample locations were chosen to provide samples representing the range of contaminant concentrations encountered at the site. The first sample location, (Well VW-11, 22 feet deep, about 65 feet from the former gasoline tank), is relatively uncontaminated, whereas the second sample location (Well VW-9, 18 feet deep, about 25 feet from the former gasoline tank) had historically yielded water samples that contained high concentrations of monoaromatic hydrocarbons but no detectable free product.

Sample collection

Ground-water samples were collected from two stainless-steel nested monitoring probes, screened at depths of 18 feet and 22 feet, respectively. These probes have a 0.25 in. outside diameter (o.d.), and are slotted over a 6 in. interval; the probes were placed in a 4 in. augered hole. Water samples were withdrawn from the probes by fitting 1/4 in. inside diameter (i.d.) silicone tubing over the probe ends and withdrawing sample by use of a peristaltic pump. The sampling probes were flushed by allowing 10 to 12 L of ground water to pass through the sampling apparatus prior to sample collection. Samples for pentane/GC-FID analysis were collected in acid-washed 250 mL brown-glass bottles fitted with a Teflon/silicone septum cap. Samples for open-loop/GC-ITD were collected in commercially prepared 40 mL vials fitted with a Teflon/silicone septum cap. Samples for open-loop/GC-ITD were collected in acid-washed 250 mL brown-glass bottles fitted with a Teflon/silicone septum cap.

Prior to being placed on ice for shipment to the lab, samples were preserved with mercuric chloride, which was added to produce a Hg concentration of 40 mg/L. Deuterated ortho-xylene was added, as a recovery surrogate, to produce a concentration of 0.20 mg/L in all open-loop/GC-ITD samples. The amount of sample submitted to the purge-and-trap device was adjusted with respect to the anticipated analyte concentration (that is, 20-400 μL). In the case of the pentane/GC-FID samples where the entire sample was extracted, water samples from wells were spiked with deuterated ortho-xylene to concentrations of 0.05 mg/L and 0.26 mg/L for the low-concentration and high-concentration wells, respectively.
Ten replicate samples were collected from each location for analysis by each technique. Collected sample volumes were approximately 250 mL for pentane/GC-FID and 40 mL for open-loop/GC-ITD analysis. Field blanks were prepared with deionized water in the field-site laboratory trailer and were spiked with deuterated ortho-xylene to a concentration of 0.20 mg/L.

**ANALYTICAL TECHNIQUES**

**Pentane/GC-FID**

In the laboratory, the 250 mL sample bottles were extracted with 2.0 mL of pesticide-grade pentane after first removing and discarding 2.0 mL of sample. The bottles were carefully resealed and inverted several times to disperse the solvent evenly throughout the sample. The bottles were then placed on an orbital shaker table and agitated for 1.5 hours. The pentane was allowed to rise to the top of the sample bottle by settling at 4 °C for 1 hour. The pentane fraction was then transferred to a 1.8 mL vial. Gas chromatographic analysis was performed on a high resolution capillary gas chromatograph equipped with a cool on-column injector and flame-ionization detector. The instrument was fitted with a 30 M x 0.32 mm DB-WAX column, with a film thickness of 0.25 µm. Chromatographic conditions were as follows: Oven: 20 °C, for 4 minutes, 4 °C per minute to 1100°C; 6 °C per minute to 175 °C; 8 °C per minute to 200 °C, 5 minute hold. Injector: 30 °C for 1 minute; 88 °C per minute to 200 °C, held for 20 minutes. Detector: 240 °C, range=1, attenuation=1. Helium carrier gas with flow controlled at 1.16 mL per minute, which corresponds to an average linear velocity of 21.4 cm/s.

**Open-loop/GC-ITD**

For open-loop/GC-ITD analysis, appropriate volumes of sample (20-400 µL) were introduced into a 5.0 mL syringe. The syringe was previously filled with an appropriate volume of interference-free dilution water, spiked with deuterated ethyl benzene (internal standard). This mixture was then injected into a liquid-sample concentrator (LSC). The transfer line from the LSC was fitted directly to the chromatographic column with a 1/16" stainless-steel union. Chromatographic separation of the sample components was performed on a 30 M x 0.25 mm DB-5 column, with a 0.25 µm film thickness. The 5.0 mL water-sample mixtures were purged with He at 40 mL/min. onto an adsorbent trap for 11 minutes. Water was selectively removed from the trap prior to desorption by ambient-temperature purging of the trap to atmosphere for a period of 5 minutes. Sample components sorbed onto the trap was desorbed onto the chromatographic column by heating the trap to 180 °C for 4 minutes. The trap was then vented to atmosphere and baked at 225 °C for 7 minutes to condition the adsorbent for the next sample. The sample components were refocused during desorption by whole-column cryofocusing, that is, cooling the entire column oven to -40 °C using liquid nitrogen. The LSC transfer line and switching valve were held isothermally at 150 °C to enable efficient transfer of material up through the C10 monoaromatic hydrocarbons. Cryofocusing and subsequent gas-chromatographic separation of the desorbed components were performed under the following conditions: Oven: -40 °C, held for 4 minutes; 50 °C per minute to 20 °C; 2.8 °C per minute to 88 °C; 10 °C per minute to 200 °C, held for 5 minutes. Helium carrier gas, pressure controlled at 11.0 lb/in², which corresponds to an average linear velocity of 30 cm/s at 200 °C column temperature. The column was interfaced directly to the ion trap detector (ITD), bypassing the open split interface, through the ITD transfer line and directly into the mass spectrometer ion source.

**RESULTS**

It was possible to identify 35 C₆-C₁₀ aromatic hydrocarbons by the open-loop/GC-ITD method compared to 21 components identified by the pentane/GC-FID method. Higher specificity (attributable to elimination of coeluting interferences, for example), sensitivity (MDL's up to 455 times lower with GC-ITD than with GC-FID) and variability (GC-ITD coefficient of variation 2.6 times higher for total C₆-C₁₀ monoaromatics compared to GC-FID) were observed for samples analyzed by the open-loop/GC-ITD method compared to those analyzed by the pentane/GC-FID method. Difficulty in resolving benzene from interferences, tentatively identified as cycloalkanes and branched alkenes, sometimes resulted in considerably higher benzene and BTEX concentrations by the pentane/GC-FID method compared to open-loop/GC-ITD. At the low-concentration sample site, mean BTEX concentrations (n=10) were 66.1 µg/L by
pentane/GC-FID compared to 490 µg/L by open-loop/GC-ITD. At the high-concentration sample site, mean BTEX concentrations (n=10) were 5,077 µg/L by pentane/GC-FID compared to 5,089 µg/L by open-loop/GC-ITD. The measured concentrations of the total C₆-C₁₀ monoaromatics were consistently in agreement between the two techniques at low and high concentrations (table 1). These measurements include 14 compounds identified by ITD/MS that were obscured by interferences or coeluting analyte peaks by GC/FID detection. Using the pentane/GC-FID technique, the coeluting components were incorrectly identified, but their contribution to the overall FID response are reflected in the reported totals.

CONCLUSIONS

Open-loop stripping followed by mass-spectrometric detection of C₆-C₁₀ monoaromatic hydrocarbons yields results that are somewhat more variable than pentane/GC-FID, but the lower MDL's of open-loop/GC-ITD are significant (table 2). The ability to identify and quantify individual components that may be poorly resolved chromatographically provides an opportunity to improve an understanding of the fate and transport of individual monoaromatic hydrocarbons in ground-water systems.

Pentane microextraction/GC-FID was generally found to yield highly reproducible data that was in good agreement with data from open-loop/GC-ITD, with the advantage of lower instrumentation costs and less complex operation. Pentane microextraction/GC-FID has the disadvantages of lower overall sensitivity and no ability to distinguish coeluting analyte peaks and interferences from target compounds. These interferences give a positive bias on reported compound levels and were most pronounced on measurements of monoaromatic hydrocarbons at low concentration sample sites.

Table 1.—Concentrations of selected C₆-C₁₀ monoaromatic hydrocarbon in gasoline-contaminated ground water at Galloway Township, New Jersey

[mg/L, milligrams per liter; GC-FID, gas chromatography-flame ionization detection; ITD, ion trap detector; C.V., coefficient of variation]

<table>
<thead>
<tr>
<th>Compound</th>
<th>Low Concentration Site</th>
<th>High Concentration Site</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pentane/GC-FID</td>
<td>Open-Loop/ITD</td>
</tr>
<tr>
<td></td>
<td>mg/L</td>
<td>C.V.</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.008</td>
<td>70.898</td>
</tr>
<tr>
<td>Toluene</td>
<td>.008</td>
<td>3.201</td>
</tr>
<tr>
<td>Ethyl Benzene</td>
<td>.045</td>
<td>4.914</td>
</tr>
<tr>
<td>O-Xylene</td>
<td>.254</td>
<td>2.851</td>
</tr>
<tr>
<td>N-Propyl Benzene</td>
<td>.137</td>
<td>3.478</td>
</tr>
<tr>
<td>1,2,4-Trimethyl Benzene</td>
<td>.615</td>
<td>3.646</td>
</tr>
<tr>
<td>1-Ethyl-2-Methyl Benzene</td>
<td>.212</td>
<td>3.182</td>
</tr>
<tr>
<td>1-Methyl Propyl Benzene</td>
<td>.009</td>
<td>3.560</td>
</tr>
<tr>
<td>1,2,3,5-Tetramethyl Benzene</td>
<td>.091</td>
<td>4.066</td>
</tr>
<tr>
<td>BTEX</td>
<td>.661</td>
<td>3.480</td>
</tr>
<tr>
<td>Total C₈ Monoaromatics</td>
<td>.645</td>
<td>3.379</td>
</tr>
<tr>
<td>Total C₉ Monoaromatics</td>
<td>1.481</td>
<td>3.634</td>
</tr>
<tr>
<td>Total C₁₀ Monoaromatics</td>
<td>.854</td>
<td>3.511</td>
</tr>
</tbody>
</table>
Table 2.—Method detection limits (MDL) for selected C₆-C₁₀ monoaromatic hydrocarbons

[FID, flame ionization detection; ug/L, micrograms per liter]

<table>
<thead>
<tr>
<th>Compound</th>
<th>Pentane/FID MDL (ug/L)</th>
<th>Open-Loop/ITD MDL (ug/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>1.36</td>
<td>0.003</td>
</tr>
<tr>
<td>Toluene</td>
<td>.739</td>
<td>.003</td>
</tr>
<tr>
<td>Ethyl Benzene</td>
<td>.322</td>
<td>.002</td>
</tr>
<tr>
<td>O-Xylene</td>
<td>.254</td>
<td>.002</td>
</tr>
<tr>
<td>N-Propyl Benzene</td>
<td>.171</td>
<td>.003</td>
</tr>
<tr>
<td>1,2,4-Trimethyl Benzene</td>
<td>.178</td>
<td>.004</td>
</tr>
<tr>
<td>1,2,3,5-Tetramethyl Benzene</td>
<td>.355</td>
<td>.004</td>
</tr>
</tbody>
</table>

¹MDL = t(N-1, 1-a = .99) X S_c

The ability to distinguish individual monoaromatic hydrocarbons in samples from ground-water monitoring wells improves the understanding of the fate and transport of hydrocarbons in ground-water systems. Use of the ion trap mass spectrometer as a chromatographic detector demonstrated distinct advantages in the measurement of trace or obscured components in these types of samples. These advantages include the ability to detect multiple components within a chromatographic peak and the ability to exclude interferences from the measured response of the target compounds. In addition the superior sensitivity of the ion-trap mass spectrometer allows the measurement of very low concentrations of monoaromatic hydrocarbons in water samples.

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Overview of Research on Use of Hydrologic, Geophysical, and Geochemical Methods to Characterize Flow and Chemical Transport in Fractured Rock at the Mirror Lake Site, New Hampshire

By Allen M. Shapiro and Paul A. Hsieh

Abstract
Research efforts at the Mirror Lake Toxic-Substances Hydrology Program research site in Grafton County, New Hampshire have focused on the development of equipment, field testing procedures, and interdisciplinary interpretive approaches of characterizing ground-water flow and chemical transport in fractured rock over distances that range from tens of meters to kilometers. This paper summarizes the results of current research in bedrock hydrogeology in local- and regional-scale investigations at the Mirror Lake site. Local-scale investigations are conducted over distances of tens of meters and focus on identification of (1) fractures and fracture properties on exposed surfaces, (2) fractures in the subsurface using borehole and surface geophysics, and (3) hydraulic and transport properties of fractures by means of hydrologic testing. In regional-scale investigations, controlled hydrologic testing cannot be conducted to identify hydraulic and transport properties of the bedrock. Regional-scale investigations have focused on (1) methods of collecting hydrologic and geochemical information in heterogeneous bedrock environments, and (2) interdisciplinary methods of synthesizing these data by ground-water-flow and chemical-transport modeling to infer hydraulic and transport properties of the bedrock.

INTRODUCTION
The U.S. Geological Survey (USGS) Mirror Lake Toxic-Substances Hydrology Program research site is located in Grafton County, at the southern extent of the White Mountains in central New Hampshire (fig. 1). The Mirror Lake site was selected for investigations in fractured rock as a part of a nationwide program to describe the fate of contaminants in subsurface environments. Although there are no known contaminants in ground water at the Mirror Lake site, the equipment, field techniques and interdisciplinary interpretive methods that are being developed in this study area are directly transferable to other fractured-rock sites where ground-water has been contaminated. Research at the Mirror Lake site is focused on characterizing ground-water flow and chemical transport in fractured rock over distances of tens of meters to kilometers. The purpose of this paper is to review the current research being conducted at the Mirror Lake site. An earlier summary of bedrock research activities at the Mirror Lake site is in Shapiro and Hsieh (1991).

SITE DESCRIPTION
Mirror Lake is located at the lower end of the Hubbard Brook valley in the southern part of the White Mountains of central New Hampshire (fig. 1). Hubbard Brook, which drains the valley, flows into the Pemigewasset River. The topography of the area generally is steep along mountain sides and flat along the Pemigewasset River. Although ground-water flow extends beyond the surface-water drainage basin associated with Mirror Lake, regional field investigations have concentrated on the Mirror Lake drainage basin. The Mirror Lake drainage basin occupies 85 ha. Land-surface elevations range from 213 m above sea level at the

Three perennial streams flow into Mirror Lake, and Mirror Lake drains through an outlet stream into Hubbard Brook.

Glacial drift overlies the bedrock in much of the Mirror Lake area. The drift thickness ranges from 0 to 55 m and consists mainly of silty and sandy till, with numerous cobbles and boulders. Kame terraces, consisting of fine- to coarse-grained sandy ice-contact deposits, are found at several levels on the mountain sides. In the area between Mirror Lake and Hubbard Brook, the silty sand and gravel form what is believed to be a delta-type deposit laid down when Hubbard Brook adjusted its grade to the Pemigewasset River during deglaciation. Mirror Lake is believed to be a kettle lake overlying a bedrock saddle, where bedrock valleys descend to the north and south. The ridge north of the lake is a moraine overlying the northern bedrock valley, where drift thickness is as much as 55 m.

The bedrock in the Mirror Lake area is a Silurian sillimanite-grade schist that has been extensively intruded by late Devonian granite (C.C. Barton, U.S. Geological Survey, written commun., 1993). The schist and granite are cut by dikes of pegmatite of unknown age, possibly a residual differentiate of the granitic intrusions. All three rocks are cut by lamprophyre dikes, whose age is believed to be middle Jurassic and early Cretaceous. At a road cut along Interstate Highway 93, directly east of Mirror Lake, the exposed bedrock consists of a complex suite of rock types. The granitic intrusions are present as dikes, irregular pods, and anastomosing fingers that range in width from...
centimeters to tens of meters. Pegmatite typically is in the form of dikes, centimeters to meters wide, that cross-cut both the schist and the granite. The lamprophyre dikes, having widths of centimeters to meters, are less common than the other three rock types in the Mirror Lake area.

All components of the hydrologic system in the Mirror Lake drainage basin are being monitored. Flow of all streams leading to Mirror Lake are measured with flumes having continuous recorders; precipitation is measured at two locations in the drainage basin; climatological information for energy budget and evaporation studies have been collected since 1983; water levels in bedrock wells, drift piezometers, and water-table wells are continuously recorded (Winter, 1984, 1985). Bedrock wells have been drilled in two clusters, referred to as the FSE and CO well fields (fig. 1). Bedrock wells also have been areally distributed in the vicinity of Mirror Lake. In early 1993, there were 13 bedrock wells in the FSE well field, 4 bedrock wells in the CO well field and 12 bedrock wells areally distributed in the Mirror Lake area. Depths of bedrock wells range from 60 to 230 m. At most bedrock-well sites, piezometers are installed at one or more locations in the saturated drift above the bedrock surface. Water-table wells, whose screens intersect the water table, have been installed throughout the watershed and at most bedrock-well sites.

Ground-water flow in the Mirror Lake area is typical of mountain-valley terranes of the New England uplands. Water from precipitation and snow-melt infiltrates into the subsurface, flows through the glacial drift and fractured bedrock, and discharges into streams, lakes and rivers. Estimates of recharge to ground water vary from 0.2 m/yr (meters per year) to 0.45 m/yr (T. C. Winter, U.S. Geological Survey, oral commun., 1993). The major features controlling ground-water flow in the Mirror Lake area are (1) the steep slope of the mountain sides, (2) the low hydraulic conductivity of the drift and the bedrock, and (3) the presence of surface-water bodies such as streams, Mirror Lake and the Pemigewasset River. In most of the Mirror Lake watershed, the water table is close to land surface, typically less than 10 m below land surface. The only exception is the moraine ridge north of Mirror Lake where depth to water table exceeds 20 m. The presence of a shallow water table suggests that local topography affects the local pattern of ground-water flow.

 Hydraulic conductivities of the glacial drift and bedrock in the Mirror Lake area have been estimated from results of hydraulic tests. Based on slug tests in piezometers, the hydraulic conductivity of the till is estimated to range between $10^{-6}$ m/s (meters per second) and $10^{-5}$ m/s (Wilson, 1991). Hydraulic conductivity of the sands in the kame terraces is approximately 10 times higher than the till. The results of single-hole, straddle-packer tests using 5-m long test intervals indicate that the bedrock hydraulic conductivity is highly heterogeneous, varying over many orders of magnitude (Hsieh and Shapiro, 1996). The average hydraulic conductivity over the upper 100 m of the bedrock is $3 \times 10^{-7}$ m/s. Single-hole tests, however, sample the rock in a small region around the bedrock well and do not necessarily represent the hydraulic conductivity controlling regional flow through the bedrock.

**CURRENT RESEARCH**

Current research at the Mirror Lake site is focused on local- and regional-scale investigations of ground-water flow and chemical transport in fractured rock. The local-scale investigations are conducted over distances of tens of meters and focus on identifying (1) fractures and fracture properties on exposed surfaces, (2) fractures in the subsurface using borehole and surface geophysics, and (3) hydraulic and transport properties of fractures through hydrologic testing (Hsieh and others, 1993). When applied individually, these methods generally yield limited information on fracture characteristics. However, when applied together, these methods become powerful tools that enable an interdisciplinary approach to the study of ground-water flow and chemical transport in fractured rock. In regional-scale investigations, controlled hydrologic testing cannot be conducted to identify hydraulic and transport properties of the bedrock. Hydraulic and transport properties must be inferred from hydrologic, geologic and geochemical information. Regional-scale investigations at the Mirror Lake site have focused on (1) methods of collecting hydrologic and geochemical information in heterogeneous bedrock terranes, and (2) the synthesis of this information by means of ground-water-flow and chemical-transport modeling.
Local-Scale Investigations

The principle problem encountered in characterizing ground-water flow and chemical transport in fractured rock is the physical identification and mathematical characterization of the heterogeneous hydraulic properties of the rock. Fractures are the conduits for fluid movement in the subsurface; therefore, identification of their location, interconnectivity and hydraulic properties is paramount in the characterization of ground-water flow and chemical transport over distances of tens of meters. Hence, a major research effort at the Mirror Lake site is the investigation of geometrical properties of fractures. Understanding the geometric properties of fractures provides a basis for making inferences and predictions of flow and transport in the subsurface. Barton (1996) conducted an extensive investigation of fracture properties and rock types on four vertical highway road cuts and one horizontal glacial pavement. Rock types were delineated, and fractures with trace lengths greater than 1 m were mapped for orientation, surface roughness, aperture, trace length, connectivity and signs of mineralization. From this investigation, the granite was shown to be more heavily fractured and to have shorter and more planar fractures than schist, whereas fractures in schist have greater fracture roughness than those in the granite. In addition, the connectivity of fractures in the granite and schist was poor in comparison to studies of fracture connectivity in other areas of the country. This investigation indicates that fluid moves through highly tortuous paths in the bedrock.

Fracture mapping is conducted only on exposed surfaces. Research on characterizing fractures in the subsurface is being conducted by means of surface- and borehole-geophysical surveys. Geophysical surveys generally yield an inferred distribution of a specific rock-mass property from which the presence of fractures must be inferred. Anomalies in the rock-mass properties attributed to fractures, however, also could be the result of variations in lithology; therefore, the correlation of several geophysical techniques as well as geologic information and hydrologic testing must be used to characterize the geometry of fractures in the subsurface.

Lieblich and others (1991) and Haeni and others (1993, 1996) discuss results of surface-geophysical surveys using azimuthal-seismic refraction and azimuthal-DC resistivity to detect the orientation of steeply dipping fractures. These methods infer the strike of a dominant, saturated, steeply dipping set of fractures from the azimuthal variation in the seismic velocity and the apparent resistivity of the rock, respectively. Azimuthal seismic-refraction data collected near the CO well field indicate that the principle strike of fractures is approximately N. 22° E.--an orientation similar to that of the principle orientation of fractures mapped on the road cut east of Mirror Lake. The principle strike of fractures on the road cut is approximately N. 30° E. Results from azimuthal-DC resistivity using a square array were conducted at the same site and yielded a similar orientation for the principle strike of a steeply dipping set of fractures. An azimuthal-DC resistivity survey using a linear array also was conducted at the same site. This survey indicated a principle fracture strike of N. 352° E. The linear array requires a large current-electrode spacing that may have emphasized environmental interferences such as a buried telephone cable. Also, voltage-electrode spacing should be large relative to the fracture spacing--a condition that may not have been satisfied at this site. The interpretation of these results indicates that multiple geophysical methods must be used to obtain an overall interpretation of fracture orientation (Lieblich and others, 1991).

The results of surface-exposure mapping indicated the importance of identifying distributions of subsurface rock types and fractures in characterizing ground-water flow. Techniques for identifying fractures and rock types in bedrock wells for hydrologic investigations are discussed by Johnson (1996) and Paillet (1996). Johnson (1996) describes the use of a borehole-color television camera to identify rock types, fractures and other conditions in the borehole, including mineralization in and near fracture surfaces. The borehole camera reduces the need to core bedrock wells to identify the distribution of rock type. Paillet (1996) discusses a systematic approach to the characterization of fractures in boreholes using a combination of standard geophysical logging tools that identify the general structure and lithology of the rock, and advanced borehole geophysical techniques that identify fractures and their potential for conducting fluid. The acoustic television log shows the location and orientation of fractures intersecting boreholes. A sensitive heat-pulse flowmeter measures the fluid velocity in the borehole. When used under ambient hydraulic conditions in the borehole, permeable fractures having different hydraulic heads in the borehole can be identified. When used in conjunction with pumping in the borehole, the location of the most permeable fractures can be identified.
Results from the heat-pulse flowmeter can also be used to infer fractures forming hydraulic connections between adjacent boreholes (Paillet, 1996). By pumping one bedrock well and measuring the fluid velocity in an adjacent bedrock well, the location of fractures responding to the hydraulic stress can be identified. Paillet and others (1992) interpreted the transient velocity response to identify hydraulic properties of fractures and propose conceptual models of fracture connectivity between boreholes.

The acoustic televiewer log and borehole television camera can identify fractures at the face of the borehole wall including their strike and dip. The distance these fractures extend into the rock and their interconnectivity with other fractures cannot be identified by these borehole methods. A major research effort at the Mirror Lake site has been the evaluation of geophysical methods that image fractures away from boreholes. Three methods of characterizing fractures in the rock mass have been applied at the FSE and CO well fields at the Mirror Lake site: single-hole, directional electromagnetic (EM) imaging; EM tomography; and seismic tomography.

Haeni and others (1993) discuss results of using a single-hole, directional EM tool that measures reflections of electromagnetic wave energy radiated from the transmitter in the tool. Water-filled fractures in the vicinity of a borehole, and fractures intersecting the borehole can be inferred from the reflected signal. The results of using this investigative tool in the CO well field showed that the same fracture zone could be detected from different boreholes, and the lateral extent and orientation of fractures could be inferred.

Seismic and EM tomography also infer the location of fractures in the rock mass away from borehole walls. Unlike the single-hole directional tool, where the transmitter and receiver are located in the same borehole, EM tomography is conducted by radiating electromagnetic energy from one borehole and monitoring its reception at an adjacent borehole (Wright and others, 1996a,b). The transmitted energy is delayed by the propagation distance and by the different dielectric properties of the water and rock matrix. By collecting data of sufficient density at a variety of angles (between the source and receiver) over the length of the boreholes, the spatial distribution of dielectric properties in the rock volume between the boreholes can be inferred by an inversion algorithm. Wright and others (1996a) also discuss the results of seismic-tomography surveys conducted between pairs of bedrock wells in the FSE well field. Seismic tomography is based on principles similar to those of EM tomography; however, instead of using electromagnetic energy, an acoustic signal is generated in one borehole, and the first-arrival of the pressure wave is monitored in an adjacent borehole. A spatial distribution of the seismic velocity in the volume of rock between the two wells can be inferred using an inversion algorithm; areas of low-seismic velocity imply zones of fracturing, and zones of high-seismic velocity imply intact rock matrix.

Wright and others (1996b) compare the seismic and EM tomograms with each other and with fractures identified from acoustic televiewer logs. Results of the seismic- and EM-tomography surveys identified the same general zones of fracturing in the rock mass in wells separated by 10 m in the FSE well field. However, the orientation of the fractures intersecting the borehole (as identified from the acoustic televiewer log) was not the same as that of the fracture zones inferred from the seismic and EM tomograms. Results of hydrologic testing confirm the orientation of the fracture zones as identified by the tomograms, implying that the orientation of permeable fractures intersecting boreholes is not necessarily the orientation of permeable zones in the rock mass.

Seismic and electromagnetic signals respond to both fractures and lithology; therefore, dielectric permittivity and seismic velocity may not correlate with hydraulic properties of the rock. Thus, tomography must be conducted in conjunction with hydrologic testing to identify permeable structures in the bedrock. The use of hydrologic testing to characterize fracture locations and their hydraulic and transport properties is another major research effort being conducted at the Mirror Lake site. Hydrologic testing, consisting of hydraulic and tracer testing, is the most direct method of investigating flow and transport properties in the subsurface. Hydrologic tests generally involve artificially inducing a perturbation (a change in fluid pressure or chemical composition) in the subsurface and measuring the resulting response. The flow metering during pumping, as discussed by Paillet and others (1992) and Paillet (1996), are examples of hydraulic testing. Hsieh (1994), Hsieh and Shapiro (1996) and Shapiro (1996) discuss hydraulic and tracer tests conducted in the FSE well field to quantify hydraulic and transport properties of the bedrock.

Hsieh (1996) and Hsieh and Shapiro (1996) discuss hydraulic tests conducted by installing inflatable packers in all bedrock wells in the FSE well field to
eliminate the artificial vertical permeability induced by open boreholes. An hydraulically isolated interval in one bedrock well was pumped continuously, and fluid pressure responses were monitored in hydraulically isolated intervals in other bedrock wells. The results of these tests indicated the bedrock does not respond as an equivalent homogeneous porous medium. Instead, there are several clusters of highly permeable fractures of limited areal extent. These highly permeable fracture clusters are only connected through less transmissive fractures.

Shapiro (1996) discusses radially converging tracer tests conducted in one of the highly permeable fracture clusters identified in the FSE well field. New equipment and field techniques of conducting tracer tests in fractured rock were developed for these tracer tests (Shapiro and Hsieh, 1996), the results of which showed that there is significant variability in rock properties that can affect chemical transport, even within a highly permeable fracture zone.

Other interpretive methods of identifying hydraulic and transport properties of the rock were developed to take advantage of environmental tracers. Goode and others (1993) used the natural variability in the radon content of water sampled during an aquifer test to estimate the effective porosity of the bedrock and the vertical leakage from the overburden. The temporal variability in radon concentration of water measured at the pumped well was attributed to the mixing of water sources; water in the glacial drift was assumed to have a different radon concentration than water in the bedrock.

**Regional-Scale Investigations**

On the scale of kilometers, hydrologic tests in fractured rocks become ineffective because, over such distances, changes in pressure caused by fluid injection or pumping are generally too small to measure, and transport times become too long for tracer tests to be practical. In order to investigate phenomena affecting flow and transport on the regional scale, the response of the ground-water system to natural perturbations and long-term human disturbances must be monitored. Monitoring hydrologic and geochemical phenomena in bedrock terranes requires the design of equipment and techniques that account for the heterogeneous hydraulic properties of bedrock.

Hsieh and others (1996) discuss methods of measuring hydraulic heads in multiple intervals in a single bedrock well. The monitoring equipment converts an open borehole to the equivalent of a multilevel piezometer. The equipment is removable, thereby allowing access to the bedrock well for hydrologic and geophysical testing when desired. The long-term installation of this equipment in bedrock wells also prevents the mixing of waters of differing chemistry because inflatable packers are used to hydraulically isolate hydraulically discrete intervals in the borehole.

Shapiro and others (1996) briefly discuss methods of collecting water samples for geochemical and isotopic analysis from bedrock wells. Because of the large variability of the hydraulic conductivity of fractures, water samples for geochemical and isotopic analyses cannot be collected by pumping an open borehole. A sample from an open borehole would yield water mixed from all permeable fractures intersecting the borehole. Instead, water samples are collected after isolating a single fracture or fracture zone in the borehole using inflatable packers.

A major research effort at the Mirror Lake site is the interpretation of geologic, hydrologic, and geochemical information to infer regional properties of ground-water flow and chemical transport in the bedrock. Rosenberry and Winter (1993) used 10 years of streamflow, lake-discharge, and climatological data to estimate the components of bedrock recharge and discharge in the water budget of Mirror Lake. Water from bedrock is estimated to account for up to 4 percent of all inflows to the lake and up to 1 percent of all outflows from the lake. These estimates are approximately 10 percent of ground-water inflows to and outflows from the lake; however, they are subject to great uncertainty because they are small relative to the major components of the water budget for the lake. These estimates of bedrock fluxes to and from the lake are being used to calibrate ground-water-flow models in the Mirror Lake drainage basin and its vicinity.

Harte and Winter (1996) used a numerical, cross-sectional-flow model of the drift and bedrock to investigate processes affecting bedrock recharge from the overlying glacial drift. Results of model simulations were compared with the distribution of the hydraulic head along an hypothesized path of ground-water flow running through the northwestern catchment area of the Mirror Lake drainage basin. The locations of bedrock recharge in the Mirror Lake area are attributed to lateral trends in the bedrock horizontal hydraulic conductivity, which is hypothesized to decrease with increasing elevations in the drainage basin to reproduce measured head gradients between the drift and bedrock.
Shapiro (1993) conducted a numerical simulation of areal (two-dimensional) regional ground-water flow in a heterogeneous bedrock terrane, where the heterogeneity was assumed to be the result of a random distribution of constant transmissivity blocks. The random distribution of transmissivity resulted in the poor connectivity of highly transmissive zones in the bedrock. The conceptual model was based on results of hydraulic testing in the FSE well field that illustrated the poor hydraulic connection between highly permeable fracture zones (Hsieh, 1996; Hsieh and Shapiro, 1996). The numerical simulations showed that hydraulic heads increased with increased elevation of upgradient locations in a manner similar to that observed in the Mirror Lake drainage basin. Thus, it is hypothesized that the poor connectivity of highly permeable zones in the bedrock could also play a role in the regional distribution of hydraulic heads.

A major research effort at the Mirror Lake site has been the analysis of ground-water chemistry and environmental isotopes to identify transport properties of the bedrock and processes affecting chemical transport in bedrock terranes over distances of kilometers. As water flows in the subsurface, its chemical composition evolves as the water reacts with the rock along the flow path. Understanding the chemical changes in ground water can help develop conceptual models of regional ground-water flow and chemical transport. In addition, environmental isotopes, such as tritium, and chlorofluorocarbons (CFC’s) in ground water can be used to estimate the residence times of shallow ground-water.

Water samples were collected from discrete intervals in bedrock wells and analyzed for a variety of dissolved solids, dissolved gases, and a variety of stable and radioactive isotopes. Busenberg and Plummer (1996) measured the concentrations of CFC’s in ground-water samples. By using historical records of CFC concentrations in the atmosphere, the date of ground-water recharge can be estimated. Drenkard and others (1996) estimated ground-water ages on the basis of the ratio of the parent-daughter isotopes tritium and helium. Many ground-water samples contained anomalously high helium concentrations; however, plausible corrections could be made for other sources of helium, and ground-water ages were estimated. The ages estimated from the tritium-helium and CFC analyses were similar. However, these ages do not correspond well with the presumed date of the maximum atmospheric tritium concentration. Both the tritium-helium and CFC ages appear to be approximately 6 years younger than ground-water ages estimated by using the maximum tritium concentration as the date of the maximum atmospheric tritium input. This difference is still being investigated and may be the result of ground-water flow through the unsaturated zone where the air phase can allow further equilibration with atmospheric conditions, or it may be a result of the mixing of waters of various ages, either naturally or through the collection of water samples.

Ground-water ages indicate the residence time of the water since it was recharged; however, the distance the water has traveled must also be identified to estimate the regional flow velocity. In heterogeneous bedrock terranes, the distance the water has traveled is not readily identifiable. Shapiro and others (1996) proposed a simple conceptual model to use changes in the concentration of the bicarbonate ion as a second measure of the ground-water-residence time in the bedrock, and as a means of estimating the average ground-water velocity in the bedrock. The model considers transport through a single fracture and diffusion of bicarbonate ions into the fracture from the rock matrix. When used in conjunction with the ground-water ages estimated from CFC or tritium-helium concentrations, an average ground-water velocity can be estimated to reproduce the measured residence time and bicarbonate concentration at sampling locations.

The basis of the conceptual model proposed by Shapiro and others (1996) stems from discussions by Wood and others (1996) regarding the significance of diffusion in defining the ground-water chemistry. Wood and others (1996) noted that residence times of less than 50 years are not sufficient for dissolution of minerals in the granite and schist along fracture faces to produce the concentration of dissolved solids in the water samples collected in the bedrock. Instead, it is hypothesized that water in the void space of the unfractured granite and schist is in chemical equilibrium with the associated minerals in the granite and schist. In particular, small amounts of calcite (1 percent by weight) have been found in samples of the granite. Thus, the equilibrium bicarbonate concentration in the rock matrix is significantly higher than the concentration in the water recharged through the overburden and into the bedrock. The concentration gradient between water in the rock matrix and water in the fractures results in the mass flux of bicarbonate ions into fractures.

Wood and others (1996) conducted laboratory experiments to identify the effective diffusion coefficient and porosity of the intact rock matrix to verify the
role of diffusion from the rock matrix. Porosity of granite samples was approximately 1.5 percent, and the effective diffusion coefficient of $^{137}$Cs in granite (including the effects of retardation, tortuosity and porosity) was approximately $6 \times 10^{-13}$ m$^2$/s. In addition, iron-staining in the rock matrix adjacent to fractures has been noted on outcrops and cores, and this is a further indicator of the effects of diffusion in the ground-water chemistry (Barton, 1996; Wood and others, 1996). Preliminary calculations of precipitation rates for ferric hydroxide using the laboratory-estimated porosity and diffusion coefficients indicate that ferric hydroxide bands can form over tens of years as the result of the diffusion of dissolved oxygen into the rock matrix. These timeframes are consistent with laboratory diffusion experiments and the variability of bicarbonate concentration in the ground water in the bedrock, which is assumed to be the result of diffusion from the rock matrix.

**SUMMARY**

Research at the Mirror Lake Toxic-Substances Hydrology Research site has focused on characterizing the physical properties that can define ground-water flow and chemical transport in fractured rock over distances that range from meters to kilometers. The characterization of ground-water flow and chemical transport over tens of meters has focused on identifying the geometrical and hydraulic properties of fractures. Mapping of surface exposures, use of surface and borehole geophysical techniques, and hydrologic testing have been used to identify properties of fractures that influence ground-water flow and chemical transport. Over distances associated with regional ground-water flow, processes affecting ground-water movement and chemical transport are inferred through the synthesis of hydrologic and geochemical data by means of ground-water and chemical-transport modeling.

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Characterizing Bedrock Fractures in Outcrop for Studies of Ground-Water Hydrology: An Example from Mirror Lake, Grafton County, New Hampshire

By Christopher C. Barton

Abstract

The fractured-rock-hydrology study site at Mirror Lake, New Hampshire provides an opportunity to use the pavement method to characterize bedrock fractures at four highway roadcuts and one glacial pavement adjacent to the bedrock-hydrology test wells at Mirror Lake. The method entails the mapping of the fracture-trace network down to fracture-trace lengths of 1 meter on a detailed geologic base map. These maps, in turn, form the basis for quantifying the scaling, interconnectedness, spatial distribution, and trace-length distribution for the fracture network. The characteristics of each mapped fracture include orientation, roughness, mineralization, aperture, and tectonic features, such as slickensides. The combined fracture data for the five pavement maps made to date indicate the following: Fracture orientation is highly variable with a preferred strike azimuth of approximately 30°E., preferred fracture dips of 7°NW., 50°SE., and 82°SE. Fracture roughness coefficients (RC) range from 0 to 18 RC values, with a mode at 5 to 6. Fracture aperture ranges from a lower cutoff of 0.005 mm to a maximum of 20.6 mm, and the frequency distribution of fractures follows a power-law function with a scaling exponent of -1.5. Fracture-trace length ranges from a lower cutoff of 1 m to a maximum of 24.6 m, and the frequency distribution follows a power-law function with a scaling exponent of -2.4. Fracture connectivity within the network is low compared to that of other sites around the country. Fracture mineralization includes iron-oxide coatings that appear have been biologically precipitated by iron-fixing bacteria in the ground water and Liesegang bands that extend up to about 1 meter into the rock matrix. A paleohydrologic map of the iron-stained fracture traces reveals that ground water flowed in only part of the available network of the open and interconnected fractures.

INTRODUCTION

Fracture networks exist in almost all rocks at or near the surface of the Earth. Where the fractures are open and interconnected, a portion of the network can conduct groundwater flow, and especially so over the short time scales associated with the extraction or injection of fluids in a bedrock well. Despite the importance of individual conductive fractures within the network, fractures are generally poorly characterized in most ground-water studies, because of the inaccessibility of buried fractures to direct observation and to the inability of surface and crosshole geophysical methods to image individual fractures and fracture networks to the same degree of detail as they can be mapped on surface exposures. Borehole logging and core sampling together permit measurement of fracture orientation, roughness, mineralization, aperture, and tectonic features. However, these characteristics may not be representative, because only a very small part of the fracture is recovered or exposed in the borehole wall or recovered in core, and statistical corrections are of limited value. It is impossible to determine fracture-trace length, spatial distribution of fracture traces and intersections, fracture connectivity, fracture abutting relations, or the size, shape, and spatial

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distribution of blocks bounded by fractures on the basis of borehole data. The primary limitation of borehole logs and cores is that they represent a one-dimensional sampling of a three-dimensional fracture network. The use of lineament analysis to attempt to locate individual fractures, fracture networks, and zones of high permeability is scientifically unsound because lineaments generally fail to coincide with fractures on the ground (Throckmorton, 1987) and because lineament analyses are highly nonreproducible because of user bias and the position of the lighting source in areal photographs (Wise and others, 1985). A recent study of the relation of lineaments and lineament intersections to the production of water in crystalline rocks shows no statistically significant correlation between lineaments and water production (Maybee and others, 1990). Studies of fractures from aerial photographs have proven to have extremely limited use in this region because of the extensive glacial cover. Of course, even with complete bedrock exposure, areal photographs provide only strike (not dip) and spatial patterns and densities. Preliminary studies at this site indicate that linear features on areal photographs do not correspond to fractures on the ground.

The purpose of this paper is to describe a method developed for directly sampling and measuring characteristics of individual fractures and fracture networks that are relevant to fluid flow in fractured rock, and that form a basis for constructing volumetric synthetic fracture networks that are conditioned to the individual and statistical properties of the fractures. The method, called the pavement method, is an integrated method applicable to sites where there are natural or excavated subplanar exposures of bedrock (Barton and Hsieh, 1989).

The U.S. Geological Survey study of flow and transport in fractured crystalline rock at Mirror Lake, New Hampshire (fig. 1) has provided an opportunity to apply the pavement method to quantify the individual properties of fractures and fracture networks in a complex geologic setting. The fracture characteristics reported in this study are the benchmarks against which results of borehole, surface, and cross-hole geophysical methods can be compared.

PAVEMENT METHOD

The basis of the method is the complete and detailed mapping of the bedrock geology and of fracture traces over a wide range of length scales on large subplanar exposures of bedrock (fig. 3). The resulting map permits characterization of properties of the fracture network including the spatial scaling of the fractures, the connectivity of the network, trace-length distribution, and fracture density; none of these properties can be quantified by geophysical or by standard methods for characterizing fractures in outcrop (Kulander and others, 1979; McClay, 1987). Where fracture staining and (or) mineralization is present, it is possible to construct paleohydrologic maps of the conductive fractures as described below. In addition to its use in constructing fracture and paleohydrologic maps, the pavement method also allows for the quantitative measurement of individual fracture characteristics, including orientation, surface roughness, aperture, staining and (or) mineralization, and any other characteristics that might be needed to determine the temporal and spatial origin and propagation of the fracture.

The pavement method has several inherent weaknesses: (1) It is only a two-dimensional sample of a three-dimensional fracture network, and (2) the apertures of individual fractures measured in outcrops are affected by unloading. The objective of a pavement study is to quantify, in surface exposures, the characteristics of individual fractures and fracture networks that are analogous to those being hydrologically sampled in the subsurface. Those who use this method must be careful not to include fractures that are caused by exposure, weathering, blasting, and stress release caused by excavation. At the Mirror Lake site, the fractures formed in the subsurface are readily identified because of their mineral coatings and precipitates from paleo ground-water flow.

MIRROR LAKE STUDY SITE

Location

The Mirror Lake hydrologic study site is located adjacent to the southwestern corner of the White Mountain physiographic province in central New Hampshire (fig. 1). The study site includes most of the Mirror Lake watershed. The study site includes very few exposures of bedrock (<2% exposure) because of a blanket of glacial deposits. The few natural exposures that do exist are small and covered with lichen and moss, making rock type, contacts, and fractures difficult to identify and measure. The
EXPLANATION
Topographic contour of altitude of land surface, contour interval is 100 meters. Datum is sea level. Wells drilled for fractured bedrock hydrology study.

Figure 1. Map showing location of the Mirror Lake fractured-rock-hydrology site, groundwater wells, and the roadcuts exposing fractures and bedrock geology along Interstate 93. Grafton County, New Hampshire.

The thickness of glacial deposits prohibits the clearing of bedrock exposures, such as those excavated in other study areas (Barton and Hsieh, 1989). However, the interstate 93 roadcut provides spectacular exposure of the same bedrock present where the hydrology test wells have been drilled immediately to the west (fig. 1). The roadcut through a small hill of exposed bedrock has produced five exposures (four subvertical faces exposed by blasting, and one subhorizontal face that was glacially cleaned and polished) that were used for purposes of mapping and studying the fractures and the geology (fig. 1). Recent quadrangle bedrock mapping by J.B. Lyons and R.H. Moench (unpublished) shows that the bedrock types of the highway roadcut underly the hydrology study site and, therefore, it is reasonable to assume that the fracture characteristics measured in the roadcut are statistically identical to fractures accessible only by drilling in the hydrology study site.

Geologic Setting

As shown on the preliminary geologic map of New Hampshire (Lyons and others, unpublished), the bedrock underlying the Mirror Lake study site lies in the Merrimack synclinorium (Central Maine Terrane). Bedrock at the site includes pelites of the upper and lower members of the early Silurian Rangeley Formation (438-428 MY (million years before present)). These pelites were multiply folded and metamorphosed during the Acadian orogeny (mid-Devonian) and attained the lower sillimanite grade (approximately 600°C and 4 kb, equivalent to burial to approximately 15km). A strong metamorphic foliation in the Rangeley Formation strikes N.25°-45°E. and dips 60°-67°NW. and 40°-80°SE. Although not shown on the preliminary geologic map of New Hampshire, the Rangeley is locally extensively intruded by dikes and by anastomosing fingers and pods of late Devonian Concord granite (370-365 MY).
Figure 2. Quantitative characteristics of fractures exposed on the I-93 Roadcut:  A. Contoured lower-hemisphere projection of poles to fractures; B. Histogram of roughness coefficient (RC) frequency for fractures; C. Histogram of aperture frequency for fractures; D. Histogram of trace-length frequency for fractures; E. Plot of trace length versus aperture; F. Ternary diagram of percentages of fracture intersection and terminations for fractures. Data from sites mapped at Yucca Mountain, Nevada and elsewhere shown for comparison.
Concord are cut by dikes and interfolial intrusions of pegmatite of unknown age that possibly are a residual differentiate of the Concord granite. All rocks are cut by lamprophyre dikes whose age is not specifically known but is likely middle Jurassic to early Cretaceous (190-95 MY) on the basis of the ages of similar dikes elsewhere in the region (McHone, 1984). As shown by Richmond and Fullerton (1991), the flanks of hills are blanketed by ground moraine of boulder till at the higher elevations and by outwash sand and gravel in the stream valleys. Locally, these deposits are as much as 10 m thick and were laid down during late Wisconsin glaciation which peaked in this region 22,000 to 12,000 years ago. The glaciation produced a limited number of bedrock outcrops by the plucking action of the ice on the lee sides of hills, the clearing of ridges, and the polishing of glacial pavements on some hill tops. The ice retreated from this region 15,000 - 12,000 years ago.

**METHODOLOGIES FOR CHARACTERIZING FRACTURES**

The pavement method of mapping and characterizing fractures and fracture networks used in this study is described in Barton and Larsen (1985), and Barton and Hsieh (1989). Each of the measured characteristics is described below, except for scaling and density, which have not yet been measured. The pavement method permits an accurate and complete sampling of the individual and network characteristics of fractures. Pavements created by blasting and removal of bedrock commonly exhibit fractures induced by blasting, stress release caused by excavation, and weathering. Such fractures show no staining and are excluded in this study.

**FRACTURE CHARACTERISTICS**

**Orientation**

Orientation has historically been considered the single most important characteristic of fractures. Where the orientation of a number of fractures is similar, they are said to form a set. When the poles to fracture planes are plotted on an equal-area lower-hemisphere projection and their concentrations contoured, as shown on figure 2A, the fracture orientations are observed to be scattered but exhibit a preferred strike azimuth of approximately 30°E. with preferred dips of 7°NW., 50°SE., and 82°SE.

**Fracture-Surface Roughness**

Fracture-surface roughness is an important characteristic because it controls the aperture variation and, thereby, the channeling of flow between the fracture walls. Fracture-surface roughness is measured where an unweathered surface can accommodate a 15-cm-long contour gauge. The roughness profiles are converted to a roughness coefficient by visual comparison to a standard set of profiles of known RC, which range (in integer values) from 0 to 20 (Barton and Choubey, 1977). RC ranges from 0 to 18 at this site, and has a mode at 5 to 6 (fig. 2B).

**Fracture Aperture**

Aperture is a major characteristic controlling the characteristics of flow in individual fractures. The functional dependence of flow rate on aperture in rough fractures is a topic of much study, as is the functional relation between hydraulic aperture and mechanical aperture. Mechanical apertures are measured on surface exposures, however, the removal of adjacent and overlying rock and exposure to surface weathering has undoubtedly affected the mechanical apertures. In contrast, apertures measured in boreholes are affected by mechanical abrasion of the drill bit and by stress redistribution and concentration around the borehole walls. It is not possible, therefore, to measure mechanical apertures that have not been so affected, either at the surface or in boreholes. Nevertheless, an imperfect measure of aperture is preferable to no measure. Scaling analysis of aperture frequency for apertures fixed at depth by mineralization (Barton and Hsieh, 1989) suggests that unloading affects the exact values, but not the form, of the aperture distribution.

A representative aperture is determined by visual inspection at places where weathering has been minimal and mineralization absent. Aperture is measured with an automotive feeler gage or a finely divided ruler. Aperture ranges from a lower cutoff of 0.005 mm to a maximum of 20.6 mm, and the frequency distribution follows a power law with a scaling exponent of -1.5 (fig. 2C).
Fracture-Trace Length

Fracture-trace lengths are measured from pavement maps or directly on the pavement surface. Figure 2D includes the exposed lengths of fractures whose traces extend beyond the edges of the pavement. Truncation affects the exact values but not the overall form of the distribution. Fracture-trace length ranges from a lower cut off of 1 m to a maximum of 24.6 m, and the frequency distribution follows a power law with a scaling exponent of -2.4 (fig. 2D). There is no discernable correlation between fracture-trace length and aperture (fig. 2E). Such a correlation might be found for isolated nonintersecting fractures, but one should not be expected for networks of interconnected fractures.

Fracture Connectivity

The fluid-flow-related properties of a fracture network are affected by the degree to which the fractures are interconnected. Fractures that are not highly interconnected can contribute only to storativity. Connectivity can be represented by the ratios of the three types of fracture termination or interaction: (1) fractures that terminate in the rock matrix (blind endings), (2) fractures that cross other fractures, and (3) fractures that abut other fractures. The percentage of blind endings, crossings, and abutments mapped at this site are shown on figure 2F. The network of fractures at this site is poorly interconnected relative to other networks mapped throughout the country, and, thus, the ground-water flow at this site is expected to be highly channelized and tortuous between wells.

Fracture Mineralization

Minerals deposited on fracture faces can be useful for determining the paleohydrology of a fracture network. All of the natural fractures (as opposed to those that were created by blasting) have coatings of iron oxide and (or) manganese oxide. Iron oxide has also penetrated as much as 1 m into the rock matrix adjacent to fracture traces, in places as a continuous band and in other places as a rhythmic series of Liesegang bands. Surface-attaching iron-fixing bacteria detected in water pumped from well FSE-6 could have been responsible for the deposition of iron oxide on the fracture surfaces, indicating that the iron oxide records the paths of paleo ground-water flow through the fracture network. The bacterial protein secretions may also have plugged the fracture permeability.

PALEOHYDROLOGIC MAP OF FRACTURE FLOW

A map of fracture traces for a part of the roadcut on the eastern side of the southbound lane of I-93 is shown in figure 3. The parts of the fracture traces shown as solid lines are coated with iron oxide that precipitated from ground water before these rocks were exposed by excavation. Note that ground water did not flow in all of the open fracture traces. The backbone is a term used in physics to denote the flow path across a percolation cluster. The term is applied here to denote that portion of the fracture network that sustained flow. In fractures where flow did occur, the direction of flow was approximately perpendicular to the plane of the map. Note that there is no percolation across the map.

![Figure 3](image_url)

**EXPLANATION**

- **--- Boundary**
- **--- Fracture trace, iron oxide staining**
- **--- Fracture trace, no iron oxide staining**

*Figure 3. Map of fracture traces exposed in I-93 roadcut. Portion of fracture traces coated with iron oxide precipitated from ground water are solid.*
SUMMARY

Pavement maps provide the basis for quantifying the scaling, interconnectedness, spatial distribution, and trace-length distribution of fractures and the fracture network. The characteristics of each mapped fracture at the study site were measured, including, orientation, roughness, mineralization, aperture, and slickensides. The fracture data for the five maps made to date indicate the following: Fracture orientation is highly variable, the preferred strike azimuth is approximately 30°E., and preferred dips are 7°NW., 50°SE., and 82°SE. Fracture roughness coefficients range from 0 to 18, with a mode at 5 to 6. Fracture aperture varies from a lower cutoff of 0.005 mm to a maximum of 20.6 mm, the frequency distribution follows a power-law function with a scaling exponent of -1.5. Fracture-trace length ranges from a lower cutoff of 1 m to a maximum of 24.6 m, and the frequency distribution follows a power-law function with a scaling exponent of -2.4. Fracture connectivity within the network is low compared to that at other sites across the United States. Fracture mineralization includes iron oxide coatings that could have been biologically precipitated by iron-fixing bacteria in the ground water and Liesegang bands that extend as much as a meter into the rock matrix. A paleohydrologic map of part of the fracture network reveals that ground water does not flow in all the available open interconnected fractures. The fracture characteristics reported here are benchmarks against which the results of borehole, surface, and cross-hole geophysical studies of fractures can be compared.

REFERENCES


Lyons, J.B., and Moench, R.H., unpublished bedrock geologic map of the Woodstock, New Hampshire quadrangle, 1:24,000 scale.


Use of a Borehole Color Video Camera to Identify Lithologies, Fractures, and Borehole Conditions in Bedrock Wells in the Mirror Lake Area, Grafton County, New Hampshire

By Carole D. Johnson

Abstract

A submersible color camera was used to describe bedrock lithologies and fractures in boreholes at the U.S. Geological Survey fractured-rock research site near Mirror Lake, Grafton County, New Hampshire. From June through August 1992, video surveys were completed in 29 bedrock wells that ranged in depth from 60 to 230 meters. Use of the submersible camera was prompted by a need to verify and provide additional descriptions of rock types identified in the wells. In two of the wells from which bedrock core was collected, video images together with drill cuttings were used to determine lithologies. These lithologies corresponded to lithologies determined directly from bedrock core samples collected from two wells. In addition, the images were used to inspect the conditions of the borehole walls for angularity, stability, or blockage.

INTRODUCTION

The Mirror Lake area is the site of a multidiscipline research effort to characterize fluid movement and chemical transport in fractured crystalline rock over a range of scales from meters to kilometers (Shapiro and Hsieh, 1991). The bedrock domain in the Mirror Lake area is typical of New Hampshire and of most crystalline rock terranes associated with orogenic belts and, therefore, is structurally complex. The bedrock is predominantly sillimanite-grade pelitic schists and gneiss that have been intruded by anatectic granites, pegmatites, and basalts (Lyons and others, 1986). Fractures that have developed in response to tectonic stresses (Hardcastle, 1989) and sheeting fractures (Trainer and others, 1987) serve as conduits for fluid movement and chemical migration. The bedrock is overlain by 10 to 50 m of glacial deposits that cover approximately 97 percent of the bedrock surface.

DESCRIPTION OF EQUIPMENT

The equipment consists of a downhole camera and light source, an electrically powered winch, control unit, and video tape recorder (VTR) and monitor. The color video camera and light source are encased in a 9.2-cm-diameter housing, which is suspended from double steel-wrapped coaxial cable. On the land surface, a powered winch is used to raise and lower the camera in the borehole. A camera control unit encodes...
the depth of the camera; processes the analog image of the borehole; and provides downhole control of the light intensity, focus, and iris (or lens aperture), all of which enhance the video image. The processed image, including a superimposed digital depth readout, is sent to a VTR and a high-resolution monitor. This camera has two light attachments that allow for two different perspectives of the well: one looking down the well and the other looking at the side of the well. In order to view and adequately record the image, the VTR should have fast and slow forward and reverse speeds, freeze frame, four heads, and a real-time counter.

CAMERA-SURVEY TECHNIQUES

Two video surveys were completed in each of the 29 bedrock wells. For the first survey, the camera was set up to look down the borehole. From this perspective (fig. 1a), the borehole wall closest to the camera lens appears at the edge of the video image, and the bottom (the more distant views) of the well appears at the center. In the actual video image, however, the bottom of the well is blocked by the light attachment, which is supported by two rods. A planar feature (such as a fracture) that intersects the borehole at 90 degrees appears as a circle, whereas a planar feature that intersects the borehole at less than 90 degrees appears as an ellipse. During the first survey, the occurrence of foliation, fractures, zones of borehole enlargement, and major changes in rock type and texture, were described. In addition, places to be closely viewed during the second survey were noted.

In the second survey, a light attachment that has a 360-degree rotational mirror tilted at 45 degrees to the camera lens to permit a side view of the borehole wall was used. A wide-angle lens directed downward toward the mirror allows a simultaneous view of the borehole wall adjacent to the mirror as well as a view down the well at the borehole below the mirror. The result is a composite image of the two views (fig. 1b). The mirror view appears at the center of the image. Surrounding the mirror view is the wide-angle view that looks beyond the edges of the mirror, and down the well, much like the perspective shown in figure 1a. This expanded view is useful when searching for individual fractures identified in the first survey or when tracing a fracture that is connected to or near other fractures. During the second survey, the rocks were viewed in greater detail than in the first survey, and more precise measurements of the locations and dips of major fractures were made.

BOREHOLE VIDEO IMAGES

![Figure 1](image)

Figure 1. Example of borehole video images: (a) Downhole view of the well at a depth of 57 meters, showing a fracture in granite intersecting the well bore; (b) Side-looking mirror view superimposed on the downhole view at a depth of 55 meters.
IDENTIFICATION OF ROCK TYPES, FRACTURES, AND BOREHOLE CONDITIONS

Rock fragments and chips diverted up the hole by the force of the air and water from the drill rig were collected and described over 1.5-m-long intervals. Although mineralogy, texture, grain size, and color of the cuttings could be adequately described, identification of rock types was difficult. Rock chips measuring 1 to 2 mm in length are not always large enough to exhibit features of the source rock, such as foliation or banding. When rock chips from a short (1- to 1.5-m long) drilling interval include chips of granite and schist, it is impossible to determine from drill cuttings whether the well penetrated a schist xenolith in a granite, a granite dike in a schist host, or a contact between two rock types. Video surveys were completed in the 29 bedrock wells to positively identify the rock types. In two of the wells from which core was collected, lithologies compiled after examination of the drilling chips and borehole video surveys corresponded to the lithologies determined directly from 100 m of bedrock core. Thus, the video images provide a direct verification of fractures and the contacts between rock types. In addition, video images can be used to describe fracture zones that are missing or completely rubbled in the bedrock core. For wells from which core was not collected, video images were used to improve the interpretation of the rock types based only on drilling logs and drill cuttings. The video images were used to describe texture, grain-size, color, presence of fractures, foliation, folds, and faults, as well as the condition of the borehole. From the video images, the borehole wall could be identified as circular, extremely enlarged, or angular and jagged. The data from the video logs were used for assessing the stability and integrity of the borehole and for planning other tests, including the placement of packers for hydraulic or solute-transport tests.

ROCK TYPES

Four major rock types (schist, granite, pegmatite, and basalt) have been identified in the bedrock outcrops, drill cuttings and video images in the Mirror Lake area. Geologic names were not assigned to the rocks encountered in the boreholes, because of the localized nature of the sampling. However, in the following list, the schist and gneiss probably correspond to the metamorphic rocks of the Rangely Formation of the Silurian age (Lyons and others, 1986). The granite is most likely anatectic, two-mica granite of the regional Concord Intrusive Suite of the Devonian age (Armstrong and Boudette, 1984; Lyons and others, 1986). These granites, derived from the melting of preexisting rocks, were injected into the overlying host rocks and commonly are found in sheetlike, tabular bodies. The basalt probably corresponds to the lamprophyric intrusions of Mid-Jurassic through Early Cretaceous age (McHone, 1984) and are found cross-cutting all other rock units.

Schists and gneisses.--Schists and gneisses are usually easy to identify by the foliated biotite, muscovite, and sillimanite. Some schist sections of the wells exhibit isoclinal folding, augens, banding, and (or) large felsic sections. Metasedimentary rocks typically are black, brown, green, yellow, or white. The coarse-grained biotites and muscovites reflect the light and appear bright and shiny, whereas fine-grained schists appear dark. In general, the schists and gneisses are much darker than the granites. The mirror attachment permitted a detailed view of some structural and stratigraphic features in the schists, such as the isoclinal fold in schistose bedding cored with a quartz layer, shown in figure 2.

Figure 2. The nose of an isoclinal fold in schist seen using the side-looking mirror at a depth of 200 meters. Bedding layers can be traced around the nose of the fold and down the limbs of the fold.
Granite.--The granite is typically equigranular, medium-to-coarse grained, leucocratic, creamy white to gray with an occasional greenish tinge. Iron staining along fracture faces and within the rock matrix can be seen clearly in some of the video images. These rocks are usually medium grained and have a sugary texture. They occasionally exhibit weak foliation of biotites and muscovites, and sometimes contain strongly foliated biotite schlieren, which are oriented parallel to major structural features in the host rock (Armstrong and Boudette, 1984). These linear features are easily visible in the video image and can usually be differentiated from fractures. Local variations in granite composition, such as increased biotite or quartz content, appear as variations in shading along the borehole wall.

Pegmatites.--Pegmatites usually are the lightest and most reflective rocks in the boreholes. The contacts between the pegmatite and their host rocks were viewed with the mirror attachment. Some contacts were sharp and straight, whereas others were graded or wavy. Large individual crystals of muscovite, biotite, feldspar and quartz were observed and their lengths measured.

Basalt.--The darkest and least common rocks in the wells are the basalts. These rocks reflect little light because of their extremely fine-grained matrix and mafic-mineral content. However, felsic inclusions, including feldspar phenocrysts and cavity fillings, are highly reflective and discernible in the video image. Basalts crosscut both the granite and the schist, are present at a variety of depths and in a variety of widths, and range from subhorizontal to subvertical. Chill margins and vesicles were viewed with the mirror attachment.

During the first survey, fractures were described as being either single fractures or as fracture zones (multiple fractures that occur over a short distance). In addition, the intersection of the fracture along the entire borehole or only part of the borehole was noted. In the second survey, the fractures were further described as being horizontal, moderately dipping, or steeply dipping. Fracture apertures were only qualitatively described as being very tight, narrow, or wide, or a fracture zone with breakout. No attempt was made to measure the fracture width. Fractures were also described for the occurrence of mineralization or mineral coatings, including iron (with some migration into the rock matrix), grayish white clay, white calcite, and light white to brownish yellow quartz. Black manganese coatings were impossible to differentiate from dark minerals.

BOREHOLE CONDITIONS

In addition to providing rock type and fracture information, the video images were used to determine borehole conditions, including roughness and angularity of borehole walls, fractures with broken-out zones or borehole enlargement, alteration of the rock mass, scoring or rifling caused by drilling, blockage of the drill hole, and possible zones of falling rocks. The borehole shown in figure 3 is no longer circular.
but is now angular, jagged, and enlarged at this fracture zone. This well was originally drilled 30 m deeper than shown, but it caved in at this fracture zone. Enlarged and angular sections of the borehole that were identified in the video surveys were avoided when placing packers for hydraulic testing, tracer tests, and long-term water-level monitoring. Information on the condition of the borehole can be used to explain the results of other borehole tests.

**SUMMARY AND CONCLUSIONS**

Video cameras are effective tools for identifying rock types, fractures, foliation, folds and enlarged zones in the boreholes. Interpretations of rock types using video logs and drill cuttings agreed with interpretations of the core. In contrast, rock types could not always be determined from analysis of drill cuttings. The video images provided information about the distribution of rock types and the extent of the fractures that was not available from previously collected data, including data obtained by conventional drilling and borehole geophysical methods. Based on these merits, video cameras are a practical method for obtaining borehole data. The interpretation of the rock types from the video surveys will be used to calibrate borehole geophysical signals.

**REFERENCES**


Fracture Detection in Crystalline Rocks, Mirror Lake Area, Grafton County, New Hampshire

By F.P. Haeni¹, John W. Lane, Jr.¹, C.C. Barton², and David A. Lieblich¹

Abstract

Six surface-geophysical methods were used to detect saturated fractures in the upper 60 m (meters) of bedrock at the U.S. Geological survey’s fractured-rock research site in the Mirror Lake area, Grafton County, New Hampshire. Crystalline bedrock, consisting of foliated schists intruded by granite, pegmatite, and gabbro, underlies 3 to 10 m of glacial drift throughout the study area. Surface-geophysical methods included azimuthal seismic refraction, azimuthal Schlumberger direct-current- (DC) resistivity, square-array DC-resistivity, inductive-terrain conductivity, very-low-frequency (VLF) terrain resistivity, and ground-penetrating radar (GPR).

Azimuthal seismic-refraction and DC-resistivity methods measured directionally dependent physical properties of the crystalline rock at the Camp Osceola well field and in a ballfield 75 m southeast of Mirror Lake. The interpretation of the seismic-refraction P-wave data is that the primary fracture strike is 022.5° (degrees) with a secondary strike at 127°. The orientation of the anisotropy and probably the fractures, as determined from a quantitative interpretation of the original P-wave data, is 037°. The interpretation of the DC-resistivity data is that the primary fracture strike is 030° with a secondary strike at 150°. Inductive-terrain conductivity and VLF-terrain resistivity data show very small anomalies that have been interpreted as possible fractures or fracture zones having a strike of 045°. Processed GPR data were used to determine the depth to bedrock and to locate numerous subhorizontal reflectors, which are interpreted to be fractures, fracture zones, and (or) foliation in the bedrock.

The strike interpreted from the surface-geophysical data correlates with the strike determined from bedrock outcrops, which are located 150 m from the Camp Osceola well field along Interstate 93. The outcrop data indicate a fracture-strike frequency maximum at 030° and a secondary maximum at 000°. Fracture dips range from 20° to 90°.

INTRODUCTION

The U.S. Geological Survey established a fractured-rock research site in the Mirror Lake area, Grafton County, New Hampshire (fig. 1) for the purpose of conducting multidisciplinary research on the flow of contaminants in fractured bedrock. As part of the study, surface-geophysical surveys to detect bedrock fractures and detailed mapping of bedrock outcrops have been conducted. This paper presents the results of surface-geophysical surveys and the mapping of fractures in bedrock outcrops in the Mirror Lake area.

Surface-geophysical methods have been used previously in a number of studies to detect saturated fractures in bedrock (Haeni and others, 1993; Lewis and Haeni, 1987). In most of these studies, a single geophysical method was used to define the predominant strike of steeply dipping fractures. The methods most commonly used were seismic refraction or direct-current- (DC) resistivity arrays rotated about a fixed centerpoint in order to measure azimuthal changes in the physical properties of the rock.
Figure 1. Location of U.S. Geological Survey fractured-rock research site and geophysical-survey sites, Mirror Lake area, Grafton County, New Hampshire. (From Haeni and others, 1993, fig. 1.)
More recent studies have used multiple geophysical methods (Lieblich and others, 1991).

For this study, surface-geophysical surveys were conducted at two sites—the Camp Osceola well field and at a field (hereafter referred to as the ballfield) located 75 m southeast of Mirror Lake, both of which are located in the Mirror Lake area, Grafton County, New Hampshire (fig. 1). At both sites, crystalline bedrock, consisting of foliated schists intruded by granite, pegmatite, and gabbro, underlies 3 to 10 m of glacial drift. Analysis of fracture data from outcrops on Interstate Route 93, located 150 m from the Camp Osceola well field, indicates a fracture-strike frequency maximum at 030° and a secondary maximum at 000° (fig. 2). Fracture dips range from 20° to 90°.

**SURFACE-GEOPHYSICAL METHODS AND RESULTS OF SURVEYS**

Azimuthal Seismic-Refraction Method

The seismic-refraction method uses an impulsive source to generate elastic waves that propagate through the subsurface. The critically refracted (head) wave, either P or S, is detected at geophones on the surface when the seismic velocity increases at depth. The effects of single fractures or small, isolated fracture zones are unlikely to be seen in P-wave refraction surveys. Azimuthal refraction methods may be able to detect an anisotropic distribution of fractures throughout the rock. For a single, saturated, steeply dipping fracture zone, a seismic-velocity maximum occurs in the direction of the fracture strike, and a seismic-velocity minimum occurs at 90° to the fracture strike. Velocity and (or) thickness variations in the material overlying the refractor can also contribute to azimuthal velocity variations. A P-wave refraction experiment that has successfully detected fractures in crystalline rocks is described in Park and Simmons (1982).

Azimuthal seismic-refraction data using P-waves were collected at the ballfield in 1990 (fig. 1) by rotating a refraction line in 022.5° -increments about a common centerpoint. For each line, a 5.7-kg (kilogram) sledge hammer served as the energy source at each shot location. Twelve vertical-displacement 7-Hz (hertz) geophones were spaced 3.1 m apart, and there were five shot points per seismic line. The near end-shot was 3.0 m from each end of the geophone line and the far end-shot was 35.1 m from each end of the geophone line. Additionally, a center shot between geophones 6 and 7 was used. A signal-enhancement seismograph was used to record the data. Elevations were recorded for each shot location and each geophone position to within 0.03 m.

Unlike some other geophysical methods used in this study, analysis and interpretation of seismic-refraction field data must be performed to obtain P-wave velocity for a given direction. For this study, velocity analysis was done using the Hobson-Overton method, developed by Scott and others (1972). The interpreted azimuthal plot of the seismic-velocity data (fig. 2) indicates a primary fracture and (or) foliation strike at 022.5° and possibly a secondary strike at 127° (Lieblich and others, 1991).

Additional seismic-refraction surveys using multicomponent shear and P-waves were conducted in 1992 as part of an effort to identify the magnitude of the true anisotropy. Preliminary results from the interpretation of a 9-component walkaway-noise survey and a radial survey indicate that the bedrock is anisotropic. A quantitative interpretation of the original P-wave data indicates that the principal direction of the azimuthal anisotropy, and probably the strike of the fractures, is 037°.

Azimuthal Schlumberger DC-Resistivity Method

The DC-resistivity method uses either a direct-current source or an alternating-current source with a frequency below 10 Hz. The current is transmitted into the ground through two electrodes, and the receiver measures the potential difference (voltage) at two other electrodes. The apparent resistivity of the subsurface can then be calculated for a specific electrode spacing and geometry. The DC-resistivity method measures the apparent resistivity of a volume of rock, which is usually large compared to the scale of and the spacing between individual fracture zones. For a single, saturated, steeply dipping fracture zone, an apparent resistivity maximum occurs in the direction of the fracture strike and an apparent resistivity minimum occurs at 90° to the fracture strike.

An azimuthal DC-resistivity survey using the Schlumberger array was conducted at the Camp Osceola well field in 1991. Data were collected every 45°, and the AB/2 spacing was expanded from 3 m to 30 m. Qualitative interpretation of these data indicate
Figure 2. Fracture strike frequency at Route 93 outcrop (upper) and seismic P-wave velocity (lower) plotted against azimuth, Mirror Lake area, Grafton County, New Hampshire. (From Haeni and others, 1993, fig. 2.)
a fracture zone and (or) foliation strike at 045°.
Azimuthal DC-resistivity surveys using the Schlumberger array also were conducted at the ballfield in 1991 and 1992. The soundings in 1991 were collected every 22.5° using a DC-resistivity system, and the AB/2 spacings were expanded from 3 m to 40 m. The soundings in 1992 were collected every 15° with an ABEM automatic sounding system, and the AB/2 spacings were expanded from 3 to 40 m. The results of the 1991 survey are shown in figure 3. The fracture strike interpreted from both data sets is 352°.

**Figure 3.** Schlumberger (upper) and square array (lower) apparent resistivity plotted against azimuth at the ballfield, Mirror Lake area, Grafton County, New Hampshire.
Square-Array DC-Resistivity Method

The square array was originally developed to take the place of Wenner or Schlumberger arrays when a dipping subsurface, bedding, or foliation was present. Techniques for analyzing the directional resistivity information provided by the square-array method were developed by Habberjam (1972, 1975). The method has not been in widespread use, but two studies that used the square array to detect fractures are described by Darboux-Afouda and Louis (1989) and Sehli (1990).

A DC-resistivity survey using the square array is conducted similarly to a traditional linear array (Habberjam and Watkins, 1967). The measurement location is at the centerpoint of the square and the array size (A) is the length of the side of the square. For depth sounding, the array is expanded symmetrically about the centerpoint, in increments of \( A/\sqrt{2} \) (Habberjam and Watkins, 1967). Major advantages of the square-array method are that the array has approximately twice the sensitivity to anisotropy as Schlumberger arrays, and the array occupies less surface area for a given depth of penetration (Darboux-Afouda and Louis, 1989). For a single zone of oriented, saturated, steeply dipping fractures, the apparent resistivity minimum measured by a square array is oriented in the same direction as the fracture strike.

Square-array data were interpreted in two different ways to determine the fracture strike—graphically (using square-array data collected every 15°) or analytically (using crossed square-array data collected every 45°). The strike was interpreted graphically by plotting the apparent resistivity for azimuthal square arrays against the azimuth of the measurement; the fracture strike is perpendicular to the direction of maximum resistivity. Graphical display and interpretation of the individual square-array data were performed on a rosette diagram using methods of Taylor and Fleming (1988). The strike was interpreted analytically by using crossed square-array data (two square arrays separated by an angle of 45°). Methods for analyzing crossed square-array data are described by Habberjam (1975).

A square-array DC-resistivity survey was conducted in the ballfield in 1992 that consisted of six square-array soundings separated by a rotational angle of 15° about the array centerpoint. The A-spacings of the arrays were expanded from 5 to 50 m in logarithmic intervals for each sounding. The data from the six square arrays show a significant change in apparent resistivity for different azimuthal orientations for all A-spacings. The azimuthal apparent resistivity values for the 50-m A-spacing (fig. 3) have a primary maximum resistivity at 120° and a secondary maximum resistivity at 060°. A graphical interpretation is that a primary fracture zone is present with a strike of 030° and a secondary fracture zone has a strike of 150°. From the data collected with the six square arrays, there are three independent crossed square-array data sets available for further analysis. Analytical interpretation of these data indicates a fracture strike at 024° and an apparent anisotropy value (the ratio of the maximum to the minimum resistivity) of 1.33.

Close inspection of the data, field site, and survey design can explain the discrepancy between the Schlumberger and square-array data, and also illustrate possible weaknesses of using azimuthal Schlumberger array surveys for fracture detection: (1) A large current-electrode separation (AB/2) is required by the Schlumberger array. This caused a buried telephone line to be included within the array that was not included within the smaller square array. (2) A large voltage-electrode separation (MN/2), as compared to the fracture spacing, is required by the Schlumberger array to detect fractures. The largest MN/2 separation used in this study was 4 m, which may not have been large enough to meet the theoretical requirements. (3) Lithologic inhomogeneities present near the voltage electrodes may have affected the Schlumberger data. In view of these considerations, the square-array results are interpreted to be more representative of the conditions at the ballfield than the Schlumberger array results.

Inductive Terrain-Conductivity Method

Horizontal and vertical dipole inductive terrain-conductivity data were collected in the ballfield along three lines oriented east-west and five lines oriented north-south. A station spacing of 0.5 m and a coil separation of 20 m was used to collect the data. Field measurements could be read to an accuracy of 0.2 mS/m. Where unstable readings were obtained, multiple readings were made and, if necessary, stations were occupied at later times.

The data were interpreted manually by looking for an anomaly typically associated with vertical conductors. The anomalies present on the lines, at this site, were extremely small (less than 0.4 mS/m) and could only be identified when multiple parallel lines
were analyzed. One possible fracture or fracture zone with a strike of 045° was interpreted from the field data.

**Very-Low-Frequency Terrain Resistivity Method**

VLF data were collected in the ballfield along three lines oriented east-west. Measurements were taken every 1 m using the Cutler, Maine and Annapolis, Maryland VLF stations. In addition, a portable transmitter with a 1 km single strand of wire was used to obtain a third data set. The data sets from the remote VLF stations were virtually identical. The signal obtained with the portable transmitter was stronger than that of the remote transmitters, and this signal was used for the interpretation. VLF anomalies were very small (less than 20 percent of the horizontal primary field), and the only way that fractures could be identified was by comparing parallel VLF data lines. Three fractures or fracture zones were interpreted from the VLF data, all with a strike of 045°.

**Ground-Penetrating Radar Method**

The ground-penetrating radar (GPR) method uses a control unit and transmitter and receiver antennas, which may be housed in the same unit, to generate and detect reflected electromagnetic (EM) waves. The advantage of GPR for fracture detection is that the conductivity and dielectric permittivity are substantially different in a fluid-saturated fracture or fracture zone as compared to those properties in the host rock. In previous investigations at other sites, Ulriksen (1982) obtained reflections from individual fractures or fracture zones in granodiorite, and Imse and Levine (1985) obtained strong scattering responses from steeply dipping fractures in carbonate rocks in northern New York.

A radar unit with a bistatic antenna configuration that operated at a center frequency of 80 MHz (megahertz) was used in this study. The antennas were towed about 30 m behind a vehicle moving at approximately 4.8 km/hr. A scan rate of 25.6 scans per second and a time scale of 900 ns was used. The gain was adjusted in the field and the signal was digitally recorded to allow for further processing. The records were marked for every 9.1 m of ground covered. Seven profiles, three east-west and four north-south, were run in the ballfield. A reflector, interpreted as the top of bedrock, is present at the top of most of the radar records. Numerous subhorizontal reflectors within the bedrock are interpreted as fractures or foliation planes, but no vertical fractures were identified.

**SUMMARY**

Six surface-geophysical methods were used to detect saturated fractures in crystalline bedrock at the U.S. Geological Survey’s fractured-rock research site in the Mirror Lake area, Grafton County, New Hampshire. Geophysical surveys were run during 1990-92 at the Camp Osceola well field and at a ballfield located 75 m southeast of Mirror Lake.

Interpreted azimuthal seismic-refraction P-wave data from the ballfield show a primary fracture (and) or foliation with a strike of 022.5° and a secondary fracture and (or) foliation pattern with a strike of 127°. The orientation of the anisotropy and probably the fractures, as determined from a quantitative interpretation of the original P-wave data, is 037°. The azimuthal Schlumberger DC-resistivity method produced inconsistent results and was shown to be less reliable at detecting fracture strike than the square-array method. The interpreted azimuthal Schlumberger data from the Camp Osceola well field showed a fracture zone with a strike of 045°, whereas the interpreted data from the ballfield showed a direction of 352°. Interpreted square-array measurements at the ballfield showed a primary fracture with a strike of 030° and a secondary fracture direction of 150°. The two electromagnetic methods, VLF terrain conductivity and inductive terrain conductivity, had very small anomalies that could only be tentatively identified as being caused by fractures (oriented 045°) when multiple lines were correlated with each other. Processed GPR data showed numerous subhorizontal reflectors that were interpreted as fractures or foliations in the rock. In addition, the depth to the top of bedrock was determined from the GPR data.

The strike interpreted from the surface-geophysical data correlates with the strike determined from bedrock outcrops, which are located 150 m from the Camp Osceola well field along Interstate 93. The outcrop data indicates a fracture-strike frequency maximum at 030° and a secondary maximum at 000°. Fracture dips range from 20° to 90°.
NOTICE

Although the information in this document has been funded wholly or in part by the U.S. Environmental Protection Agency under interagency agreement DW14935104 to the U.S. Geological Survey, it does not necessarily reflect the views of the U.S. Environmental Protection Agency, and no official endorsement should be inferred.

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Use of Well Logs to Prepare the Way for Packer Strings and Tracer Tests: Lessons from the Mirror Lake Study

By Frederick L. Paillet

Abstract

Although well logs can never replace conventional aquifer-testing techniques, a carefully designed suite of borehole measurements can identify the distribution of fractures along well bores. This information can be used to improve the effectiveness of hydraulic testing and water sampling. After nearly a decade of logging research at the Mirror Lake site, we have developed a combination of conventional and new techniques that have proven especially effective in preparing the way for subsequent installation of packer strings and tracer-test analysis. The approach consists of four steps: (1) characterizing the general structure and lithology of the rock mass by interpreting conventional well logs, (2) identifying and characterizing individual fractures by obtaining acoustic televiewer and other borehole image logs, (3) identifying the few fractures intersecting the well bore that produce water during pumping by running high-resolution flow logs in pumped and observation boreholes, and (4) inferring the pattern of fracture connectivity in the rock mass adjacent to boreholes by analyzing transient flow in boreholes at carefully selected locations between producing fractures. The application of this analysis allows geochemists and hydrologists to identify those locations where packers can be set to prevent communication between conductive fractures and to design efficient procedures for otherwise time-consuming aquifer and tracer tests.

INTRODUCTION

Fractured-bedrock formations are some of the most heterogeneous aquifers investigated in studies of toxic-substance dispersal in ground water. Characterization of a fractured formation requires extensive series of water-sample analyses, straddle-packer injection tests, and tracer studies to infer the complicated three-dimensional distribution of transmissivity within the rock mass. The problem confronting the hydrologist is especially complex where boreholes encounter numerous fractures, all of which potentially can communicate with each other in an open borehole. Preliminary study is needed to identify the specific depths in boreholes where a limited string of packers can be used to isolate the primary flow zones.

The U.S. Geological Survey has been conducting a long term study to develop new analytical techniques for applying borehole geophysical logging to the characterization of fractured-bedrock aquifers at the Mirror Lake site. Since this study began in 1984, logs have been run in 17 boreholes at two borehole arrays and in 12 isolated boreholes scattered over the study area (fig. 1). This report reviews the suite of conventional and recently developed experimental logs that has been developed for the specific purpose of preparing the way for subsequent packer installation and tracer tests. Well logging is important in this regard because it provides quick and efficient characterization of the fracture distribution along the well bore, identification of the very few hydraulically important fractures that are connected to large-scale flow paths, and information concerning the possible connections between those flow paths in the adjacent rock mass.

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Figure 1. Location of isolated boreholes and the Forest Service East (FSE) and Camp Osceola (CO) borehole arrays at the Mirror Lake, New Hampshire fractured rock study site.
Conventional borehole geophysics (well logging) is useful in defining the general lithology of rock masses penetrated by boreholes, but is not very useful in identifying individual fractures. Caliper logs indicate those intervals where the borehole is enlarged by fracturing. Natural gamma logs indicate where fractures could be associated with lithologic contacts or where radioisotopes could be deposited as partial fracture fillings. Epithermal-neutron, electrical resistivity, and acoustic logs indicate where rock properties have been altered adjacent to fractures. All of these logs sample rock properties over volumes too large to be affected by fracture permeability directly, but each of these logs provides useful indications of the direct (mechanical weakening) and indirect (alteration) effects of fractures on the bulk properties of rocks (Keys, 1979; Paillet, 1993a).

The acoustic borehole televiewer (BHTV) log is a device that produces a photograph-like image of the borehole wall by recording the intensity of ultrasonic reflections from the borehole wall (Zemanek and others, 1970; Keys, 1979). The images produced by the BHTV system can be used to identify the strike, dip, and relative size of fractures that intersect the borehole; however, the BHTV system characterizes fractures only in the immediate vicinity of the borehole wall where the appearance of the fracture has been affected by drilling.

The heat-pulse flowmeter (HPFM) is a high-resolution flowmeter designed to measure vertical flows in well bores over the range of 0.04 to 10 L/min (Hess, 1986). Flows are measured by recording the time interval between the electrical generation of a small parcel of heated water in the measurement section of the tool and the arrival of that pulse at a thermistor located 2 cm above or below the heat source. Profiles of the vertical flow in boreholes are generated by measuring flow at discrete depth points where the tool is held stationary and a downhole bladder is inflated to fill the annulus (Hess and Paillet, 1990). The flowmeter is used to measure flow produced by the influence of naturally occurring differences in hydraulic head between fractures intersected by the borehole, and the changes in that flow field produced by pumping from one of the boreholes in the well field.

The analysis of fractured rock aquifers developed over the course of the Mirror Lake study consists of four steps: (1) identification of the general structure and lithology of the host rock formation, (2) identification and characterization of the fractures intersecting the borehole, (3) identification of fractures conducting flow during cross-borehole aquifer tests, and (4) development of specific hydraulic models for flow paths between boreholes based on changes in the flow field over time during cross-borehole flow tests.

Geophysical well logs can be used to determine the general structure of a rock mass, and BHTV image logs can be used to identify the distribution of fractures along the well bore. These applications of logs are illustrated schematically in figure 2A and 2B, and are described in detail by Paillet (1991a), Paillet and Kapucu (1989), and Keys (1979). The results are especially effective when logs indicating alteration, such as the resistivity log, are compared to image logs, such as BHTV, that show how the patterns of alteration are related to specific sets of fractures. As indicated in the figure, these results can be useful in inferring the locations of unaltered and unfractured intervals that could be used to isolate fracture zones from each other.

Numerous studies have shown that only a small subpopulation of fractures conduct flow during aquifer tests, and that fracture connectivity is more important in controlling the distribution of flow than local fracture aperture (Paillet, 1991b; Long and others, 1982). High-resolution flow measurements made with the HPFM during borehole pumping, or in observation boreholes when an adjacent borehole is pumped, are very effective in identifying those few fractures conducting flow during aquifer tests or cross-borehole flow tests (fig. 2C). Even when the depths of fractures conducting flow into or out of pumped and observation boreholes are known, it is still not known how those fractures are connected to allow flow through the surrounding fractured rock. Some of these connections can be inferred by correlating fractures and fracture zones between boreholes or by projecting inflow and outflow points identified during aquifer tests across the borehole array. Such projections are described in detail by Paillet and others (1987) and Paillet (1991a). This technique has been expanded to address the transient evolution of the measured flowfield during the course of cross-borehole flow tests. For example,
Figure 2. Schematic illustration of fracture characterization: (A) two fracture zones intersected by the pumped and observation boreholes; (B) caliper, televiewer, and electrical resistivity logs for the observation borehole; (C) vertical-flow profiles obtained during cross-borehole flow tests used to define locations where water enters and exits boreholes under ambient conditions, shortly after the pumping begins (early), and after pumping for more than 1 hour (late); and (D) transient flows measured at specific depths in the observation borehole during repeated aquifer tests.
previous results have shown that the vertical profile of flow varied with time during cross-borehole flow tests (fig. 2C). Flow transients can be measured by continuously recording the variation in flow measured when the experiment is repeated with the flowmeter stationed at specific depths (a, b, and c in fig. 2C). These transient flows conform to certain type curves (Paillet, 1993b) such as those illustrated in figure 2D.

**TRANSIENT-FLOW TYPE CURVES AND ANALYSIS**

The type-curve analytical technique developed from the Mirror Lake study is based on the recognition of characteristic flow responses for measurements made in casing above all fractures that intersect the well bore and measurements made between pairs of fractures communicating with each other along the open borehole during the course of the experiment (fig. 3). Transient-flow curves of type a (fig. 3) are obtained when measurements are made in casing. These transients are characterized by a maximum flow ($Q_{max}$) and a time interval required to achieve that maximum ($\Delta T$).

Interaction between the two sets of conductive fractures is determined by the shape of the type curves for flow along the well bore at measurement station b (type curves $b_1$, $b_2$ and $b_3$ in fig. 3; Paillet and others, 1992). If the two sets of fractures do not communicate with each other in the rock mass between the two boreholes, the flow transient will build up to a quasi-steady value as in type curve $b_1$. However, if there are permeable connections between the two fractures in the intervening rock mass, the quasi-steady flow will not be achieved and a flow transient similar to type curve $b_2$ will be measured. In the extreme situation where the two fracture zones are short-circuited in the intervening rock mass, type curve $b$ will be exactly proportional to type curve a (type curve $b_3$ in fig. 3).

Two field examples of these type curves are given in figure 4. In figure 4A, the flow in the open hole between boreholes matches type curve $b_1$, indicating that the two fractures are completely isolated in the surrounding rock mass. However, the flow in the open borehole is similar to type curve $b_3$, in figure 4B indicating that the two fractures are short-circuited near the well bore. The strange shape to the transient measured in casing in figure 4B represents a pump failure during that phase of the aquifer test and not a departure from the expected type curve.

Although these results seem clear-cut and useful, one note of caution is warranted. The analogy between flow-transient type-curve analysis and standard hydraulic tests is clear, but the transient measurements are made in the presence of open boreholes. The well-bore storage and communication along the open boreholes in the well field affect these measurements just as much as they affect conventional aquifer tests. The flow-transient analysis could be improved by installing packers at appropriate locations in all of the open boreholes; this technique will be explored in future studies. Even without such measures, we find the flow-transient technique useful in making a
A systematic approach to fracture characterization using borehole geophysics has been developed over nearly a decade of geophysical logging in open bedrock boreholes at the Mirror Lake study site. One of the most important applications of these logging techniques is conducting a preliminary investigation of fracture hydrology so that fracture zones can be isolated with packers soon after boreholes are drilled. The information obtained during this preliminary investigation is also helpful in planning efficient and effective aquifer tests and tracer studies.

The fracture-characterization approach developed during the Mirror Lake study consists of four steps: (1) using conventional geophysical measurements such as caliper, temperature, gamma, neutron, resistivity, and acoustic logs, to characterize the general structure and lithology of the rock mass along the well bore; (2) using borehole image logs, such as the televiewer to indicate the characteristics of individual fractures intersecting the borehole; (3) using high-resolution flow measurements to identify fractures that conduct flow during aquifer tests; and (4) using data obtained during the transient evolution of the flow field during aquifer tests to infer the boreholes. These techniques have proven effective in quickly and efficiently identifying depths where a few packers can be used to isolate the major flow zones within the aquifer. The transient-flow analysis can be used to infer whether fractures conducting flow into or out of observation boreholes during aquifer tests are completely isolated from each other in the surrounding rock, or whether there is a hydraulically conductive fracture connection between these two fractures. Although this suite of geophysical measurements will probably never replace conventional aquifer tests, the application of these techniques in the Mirror Lake study indicate that an effective borehole logging program began immediately after boreholes are drilled can greatly improve the effectiveness of subsequent hydraulic tests and tracer studies.

**REFERENCES**


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**Figure 4.** Examples of transient-flow response when the pumped well intersects a single major fracture zone, and the observation borehole connects the primary fracture zone with a deeper fracture zone: (a) example where the secondary zone is hydraulically isolated from the primary fracture zone; (B) example where the secondary zone is hydraulically connected to the primary fracture zone.

preliminary evaluation of fracture connectivity within a few days after boreholes have been drilled. The speed with which these measurements can be made indicates that the results will be useful in the subsequent design of conventional but much more time-consuming hydraulic tests such as those described by Hsieh and others (1987), and Shapiro and Hsieh (1991).

**SUMMARY**

A systematic approach to fracture characterization using borehole geophysics has been developed.


Velocity, Attenuation, and Dispersion Electromagnetic Tomography in Fractured Rock

By David L. Wright¹, Gary R. Olhoeft¹, and Thomas P. Grover¹

Abstract

Hole-to-hole electromagnetic tomography data have been acquired from 15 pairs of wells at the Mirror Lake site, Grafton County, New Hampshire, using a high-speed borehole radar system designed and built by the U.S. Geological Survey. Although tomography has good theoretical and mathematical underpinnings, higher resolution, better data-acquisition methods, better tomographic processing and better visualization of the processed data than are currently available are needed if tomography is to achieve full potential as a geophysical tool for hydrologists. A 3-dimensional display of two velocity tomograms from data collected at the FSE well field at the Mirror Lake site illustrates the potential for mapping fracture zones in three dimensions. In addition, we show examples of velocity, attenuation, and dispersion tomograms made from a single data set in the well pair FSE4-FSE1. Comparisons between these three tomograms and with projected fractures from acoustic televiewer logs indicate that velocity, attenuation, and dispersion tomograms, though having some correlations with each other and with fractures, differ in shape. Because tomograms respond to lithology as well as to fractures, it might be necessary to use more than one type of tomogram to help discriminate between the response to fractures and the response to lithology in tomograms, unless the lithology is uniform.

INTRODUCTION

A radar/tomography system incorporating a high-speed digital-data-acquisition system has been designed and built by the U.S. Geological Survey (USGS) (Wright and others, 1989; Wright and others, 1990). This system has provided the digitally recorded data from which hole-to-hole tomograms for fracture mapping at the Mirror Lake site, Grafton County, New Hampshire (fig. 1) have been produced. The geohydrologic setting of this area is given in Winter (1984). The rock from wells FSE4 and FSE1 is largely granite, pegmatite, and schist (C.D. Johnson, U.S. Geological Survey unpublished data in Bow, N.H. office). The tomograms were produced with software written at the USGS (Olhoeft, 1988). The objective of this paper is to illustrate similarities and differences between velocity, attenuation, and dispersion tomograms and point out the need to examine all three types of tomograms for correlation with fracture and lithologic information to help hydrologists in their research, the objective of which is to develop improved 3-dimensional (3-D) hydraulic flow models for fractured rock.

EQUIPMENT AND METHODS

The data from which we are producing electromagnetic tomograms were obtained with a hole-to-hole short-pulse system. A short-pulse transmitter, for which the peak in the amplitude spectrum is at 60 megahertz (MHz), radiates energy through the volume of rock to be studied. In the rock at Mirror Lake the wavelength at 60 MHz is about 2 m. The waveform is retarded in time, in response to increases in dielectric permittivity; attenuated in amplitude, in response to increases in electrical conductivity; and broadened in time in response to frequency dependent processes such as scattering. We record data while the transmitter

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Figure 1. Location of the FSE well field at the Mirror Lake site, Grafton County, New Hampshire.
and receiver are moving, typically at 12 cm/s (25 ft/min). At this speed, we average 512 waveforms and record at 17-cm intervals. The transmitter and receiver move in synchronism in their respective boreholes at offsets of 0, +5 m, -5 m, +10 m, and -10 m. Other offsets or methods of data acquisition are possible with the system. The full waveform is displayed on a color monitor in real time and recorded on a high-capacity magneto-optical disk drive.

DATA PROCESSING

After the data are acquired, the waveforms are picked automatically for first arrival time, amplitude, and first-cycle width. The picked data must be supplemented by accurate survey and borehole deviation data to produce quality tomograms. To determine the quality and consistency of the entire data set, the first arrival times are used with the measured surface positions and borehole depth/deviation data to perform a consistency test (Olhoeft, 1993). The raypath distance divided by the first arrival time is the average velocity of electromagnetic propagation between the boreholes. The square of the ratio of the speed of light in vacuum to this velocity is the relative dielectric permittivity. For each offset between transmitter and receiver, the apparent relative permittivity is computed using first arrival time and raypath distance for the perturbed receiver-tool position. A set of curves for five offsets is generated. These curves are the average for the entire hole-pair data set. If the data set is consistent and there are errors neither in instrument timing nor in knowledge of the tool positions, the five curves should intersect where the probe deviation equals zero and at the average relative permittivity of the medium. In practice, some error occurs, so there is a spread in the intersections of the five curves. The spread is an indication of the quality of the overall data set (fig. 2).

For the FSE4-FSE1 data set the spread is small (all curves cross inside one unit square) indicating that the data are consistent, but there is a cumulative positioning indicated error of about 2 m. The cumulative positioning error is the sum of all surveying errors, borehole-deviation measurement errors, and tool-positioning errors. The picked data are then processed using a filtered back projection algorithm (Olhoeft, 1988) to produce the following tomograms. The tomograms can be displayed on a workstation or personal computer in 3-D, and rotated, tilted, and zoomed in real time as an interpretive aid.

TOMOGRAMS AND FRACTURES

As noted previously, a radiated electromagnetic pulse is modified by the electrical properties of rock and water as the pulse propagates through fractured and/or inhomogeneous rock. Three processes are easily distinguished and can be measured from recorded data. The first process is first-arrival-time retardation. First arrival time is proportional to the distance between the transmitter and receiver and inversely proportional to average velocity. Velocity is inversely proportional to the square root of the relative dielectric permittivity, defined above. Because unfractured crystalline rocks, such as granites, commonly have relative dielectric permittivities in the range of perhaps 5 to 7, whereas water has a relative dielectric permittivity of about 81, it is expected that fracture zones containing significant amounts of water will manifest lower electromagnetic wave velocities than adjacent unfractured rock. Therefore, a velocity tomogram might be expected to image the location and the relative amount of water in fracture zones. The greater the proportion of water in a given volume of rock, the slower the velocity. Thus, in a velocity tomogram, we expect that local velocity minima might indicate the presence of water-filled fractures. Velocity tomograms are presented in figures 3 and 4a and discussed later in this paper.

A second process is attenuation. As a pulse propagates through rock, it is diminished in amplitude both by geometrical "spreading loss" and by ohmic losses in the rock that convert electromagnetic energy to heat. Electrical resistivity, or its reciprocal, conductivity, controls ohmic loss. The higher the resistivity, the lower the loss. Unfractured crystalline rock can have resistivities of thousands of ohm-meters, whereas water, unless it is very fresh, will commonly be in the tens to low hundreds of ohm-meters. Thus, it might be expected that an attenuation tomogram would image the presence of fractures by areas of high attenuation. The terms "high" and "low" here are relative to the particular rock being imaged. The calculated numerical values that produce a tomogram are not as important as the variations of those values that produce the visual image.

The third process is dispersion, manifested by broadening of the radiated pulse shape as the pulse propagates through a dispersive medium. It is common to define a dispersive medium to be one in which the phase velocity is a function of frequency. In practice, however, any process that removes energy from a
Figure 2. Relation between relative dielectric permittivity and cumulative transmitter-receiver tool position errors for transmitter-receiver offsets of 0, +5 m, -5 m, +10 m, -10 m for well pair FSE4-FSE1. The spread in the intersections of these five curves is a measure of the consistency of the data set. The average relative dielectric permittivity is 6.55 with error bars of +/-0.24. The average cumulative tool position error is -2.04 m.

In this paper, we merely assert, based on experimental observation, that dispersion, as well as velocity and attenuation, can usefully correlate with fractures.

A complicating factor for the interpretation of tomograms is that rocks themselves are rarely spatially homogeneous even within a single rock type such as granite, and if the rock encountered by a pair of wells is not all of the same type, as it is not in wells FSE1 and FSE4, the resulting heterogeneity in electrical properties that will be imaged by a tomogram may be indicative of lithology, fracturing, or both. An additional complication is that the presence of water-filled fractures does not always translate into high transmissivity, as has been pointed out by Paillet (Paillet and others, 1987; Paillet and Kapucu, 1989; and Paillet, 1991), who...
Figure 3. A pair of velocity tomograms in well pairs FSE1-FSE2 and FSE2-FSE4. The arrows indicate a zone that is known to have fractures with high hydraulic transmissivity. The large cube is 100 meters on a side and the grid is at 10 meter intervals. The gray scale goes from dark (low velocity) to light (high velocity).

has noted that large fracture apertures as measured with the acoustic televiewer do not always have high hydraulic transmissivity. Despite these complications, however, tomograms imaging rock electrical properties between wells at Mirror Lake do correlate with zones containing fractures of high hydraulic transmissivity.

Figure 3 shows a pair of velocity tomograms between well pairs FSE1-FSE2, and FSE2-FSE4 that successfully image zones of fractures known to have high hydraulic transmissivity. These well pairs are at right angles to each other, so the view is into the tomograms as if looking into the pages of a half-opened book. The large cube is 100 m on a side, and the grid intervals are 10 m. The velocity gray-scale runs from dark (slow) to light (fast). The terms "slow" and "fast" are relative to the global average velocity in the tomogram. The actual values are not very important to the
Figure 4. Three tomograms produced from the same data set between wells FSE4 (left) and FSE1 (right): (a) a velocity tomogram, (b) an attenuation tomogram, and (c) a dispersion tomogram. For this case it appears that (a) correlates best with the fractures that have high hydraulic transmissivity (marked with arrows). In each tomogram the gray scale is from dark (low) to light (high).
question of whether the tomograms visually image fracture zones. The arrows indicate the location of a zone that contains hydraulically permeable fractures (Paillet, 1991).

Figure 4 shows three tomograms produced from the same data set taken between wells FSE4 (left side of each panel) and FSE1 (right side). Figure 4a is a velocity tomogram formed from first arrival time picks, figure 4b is an attenuation tomogram formed from amplitude measurements, and figure 4c is a dispersion tomogram formed from pulse-width measurements. Superimposed on the tomograms are projections of fractures determined from acoustic televiewer logs of holes FSE4 and FSE1 (Paillet, 1991; Wright and others, 1996). The fractures seen in well FSE1 were projected in the plane defined by the FSE4-1 pair halfway to well FSE4 and the fractures in well FSE4 were projected half way to well FSE1. The overlays are inexact because the tomograms include the effects of well deviation, and are therefore wider at the bottom that at the top, whereas the fracture projections neglect well deviation. Approximately 0.5 meter zones along each well have been excluded from each tomogram because calculated values immediately adjacent to the wells are not considered reliable. The gray scale runs from low to high in each tomogram. The actual calculated values for velocity, attenuation, or dispersion are not particularly important for the purpose of identifying visual correlations with fractures and thus have been omitted. According to Paillet, the projection angles are subject to errors of a few degrees, and it appears that relatively few fractures project very far in the FSE well field. Thus, the indicated projections are not definitive, but comparisons of projected fractures to the tomograms is of considerable interest. When well FSE4 is pumped and a flowmeter is used to find fractures that carry significant flow, it is determined that there are two fractures in well FSE1 and two in well FSE4 that have much higher hydraulic transmissivity than any other fractures. The projections of these fractures are denoted by the heaviest lines. The two fractures intersecting well FSE4 that have the highest transmissivity are in the 39 to 47-m deep zone. Of these, 80 percent of the water flows through the upper fracture. Consider the zone from 39 to 47 m deep in the tomograms. In this zone, the velocity tomogram (fig. 4a) seems to be responding to the presence of the fractures. Presumably there is more water in this zone than in adjacent zones. The attenuation tomogram (fig. 4b) shows an increase in attenuation in this zone compared to the attenuation in the area below, but the local attenuation maximum is several meters above this zone. The dispersion tomogram has only subtle features in the region of the high-transmissivity fracture projections, but strong sharp features in other regions may correlate with other fractures.

CONCLUSIONS

Electromagnetic tomograms map changes in electrical properties. The presence of water-filled fractures will alter the local electrical properties, but so will lithologic differences. The tomograms presented here show correlation with some projected fractures but not others. In addition, the presence of water-filled fractures does not, in itself, produce high hydraulic transmissivity. Consequently, we believe that cross-borehole tomography will be a valuable tool for characterizing and mapping fractures, but must be used in conjunction with other geophysical measurements to achieve its full potential. We also conclude that more than one type of tomographic processing might be needed if we are to improve the ability to separate the effects of lithology from those caused by the presence of water-filled fractures.

ACKNOWLEDGMENT

We acknowledge F.L. Paillet for providing fracture projections from wells FSE1 and FSE4 and for providing digital data for fractures mapped with the acoustic televiewer in all of the FSE wells.

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Electromagnetic and Seismic Tomography Compared to Borehole Acoustic Televiewer and Flowmeter Logs for Subsurface Fracture Mapping at the Mirror Lake Site, New Hampshire

By David L. Wright¹, Gary R. Olhoeft¹, Paul A. Hsieh², Ernest L. Majer³, Frederick L. Paillet¹, and John W. Lane Jr.⁴

Abstract

Among the techniques used in research at the Mirror Lake site, Grafton County, New Hampshire, are electromagnetic (EM) and seismic tomography, borehole radar, borehole acoustic televiewer, and borehole flowmeter. Of these techniques, tomography and radar can probe several tens of meters between or around boreholes at that site with resolutions in the order of 1 meter, whereas televiewer data provides great detail at the borehole wall but little penetration. Flowmeter data, along with hydraulic tests and tracer tests provide information on hydraulic connectivity, but hydraulic paths between the wells can not be inferred from these data alone. We find from side-by-side comparison of electromagnetic and seismic tomograms of rock properties between wells FSE1 and FSE4 that both types of tomograms show the presence of fractures of high hydraulic transmissivity. We present velocity tomograms for two EM systems and one seismic system, attenuation tomograms for the two EM systems, and projections of fractures derived from acoustic televiewer logs. The pulsed transmitters used in the EM tomography at Mirror Lake produced wavelengths in the granite of about 2 m. The seismic system produced wavelengths of about 1 m. Seismic and EM tomography can detect the presence of fractures whose aperture is much smaller than a wavelength but can not resolve fractures whose spacing is much less than the wavelength. Resolution—the ability to distinguish two nearby objects from one another—is determined by a number of factors, including spatial data density, but resolution usually can not be better than about half the wavelength used for probing regardless of whether the method is EM or seismic. It is possible to achieve some resolution improvement in low-attenuation environments, but a needed step to achieve maximum benefit from tomography is correlation of the tomograms with other hydrologic and geophysical information. Tomography is an art that is not fully mature but can be expected to improve in the future.

INTRODUCTION

Data have been recorded between 15 pairs of wells in the FSE field (fig. 1) with the radar/tomography borehole system developed by the U.S. Geological Survey (USGS) (Wright and others, this proceedings), and 18 pairs have been examined with a hole-to-hole seismic tomography system developed by Lawrence Berkeley National Laboratory. In addition, one pair of wells was studied tomographically using equipment leased from ABEM, a Swedish company. Because it was of some interest to compare results from three systems, all three were run
in the well pair FSE4-FSE1. This afforded a rare opportunity to see results in the same pair of wells that were obtained by different systems and processed by three independent groups by means of three different sets of software. Results of the borehole acoustic televiewer, flowmeter, and packer tests, which indicated the presence of the high-transmissivity fractures, were compared to the tomograms. The tomographic studies at Mirror Lake are intended to aid hydrologists in the development of adequate 3-dimensional fracture-flow models, suggest other hydrologic applications of tomography, indicate limitations for applications of tomography in its present state in fractured crystalline rock, and identify directions in which the state-of-the-art could be enhanced for toxic-substances hydrologic studies.

Figure 1. Location of the FSE well field at the Mirror Lake site in central New Hampshire. The geohydrologic setting of this area is given in Winter, 1984.
Figure 2. Generic tomography schematic for electromagnetic or seismic tomography. The number, spacing, and relative locations of the transmitter and receiver stations may vary.

BASICS OF TOMOGRAPHY

Tomography between boreholes is conceptually and mathematically similar to what is done when a medical computer-aided-tomography (CAT) scan is made, but the distances covered in borehole applications are much greater, the angular coverage is incomplete, and the resolution is much lower. The method of collecting data from boreholes is to record a number of measurements with a transmitter and receiver or string of receivers at various locations so that a number of raypaths pass through any particular volume of rock (fig. 2). For any given raypath, an average number for velocity, amplitude, or some other quantity is measured. If a water-filled fracture zone is present, it would be expected, for example, that the velocity would be lower for both electromagnetic (EM) and seismic waves than it would be in unfractured rock. Mathematical algorithms are applied to calculate an array of values for the mapped quantity at particular locations in the rock. The region between two boreholes is gridded, and calculated values are assigned to each area element, commonly referred to as a pixel. Frequently a smoothing algorithm is applied to visually enhance the display. The display can be presented by using a color scale, a gray scale as in figures 3 and 4, contouring, or some combination of methods. Many algorithms are used for producing tomograms. Each has strengths and weaknesses. Much of the literature on tomography is dominated or motivated by medical applications (Herman, 1980). Applications of tomography to geophysics has grown rapidly, however, and there is now a substantial and growing literature applicable to geophysics (Dines and Lytle, 1979; Natterer, 1986; Kak and Slaney, 1988). There is still much art involved in producing tomograms. A "good" tomogram will be well constrained by the data from which it is derived and will visually reveal features of interest to the hydrologist, geologist, or geophysicist. Things that might be of great interest to the geologist, such as lithology, may be of less interest to the hydrologist who wants to know where the fractures are between wells and which fractures are hydraulically connected, and to quantify the hydraulic conductivity. A good tomogram from the hard-rock fracture-flow hydrologist's point of view will need to help answer those questions.
Figure 3. Electromagnetic velocity tomogram produced with the ABEM system (a), electromagnetic velocity tomogram produced with USGS system (b), seismic velocity tomogram produced with the Lawrence Berkeley National Laboratory system (c).

EXPLANATION
The location of fractures that have high transmissivity
Figure 4. Electromagnetic attenuation tomogram produced with the ABEM system (a), electromagnetic attenuation tomogram produced with the U.S. Geological Survey system (b), fracture projections produced from the acoustic teviewer logs (c). The fractures with high hydraulic transmissivity are indicated with heavy lines.
EQUIPMENT AND MEASUREMENT METHODS

The ABEM radar system transmitter used in this study radiates a short pulse whose amplitude spectrum peaks at about 60 MHz. The transmitter was in well FSE1 and the receiver was in well FSE4. Data were recorded with the transmitter and receiver stationary at 3-m intervals.

In the case of the USGS radar, the 60-MHz transmitter (not identical to the ABEM transmitter) was in well FSE4 and the receiver was in well FSE1. Theoretically, the same system should produce identical tomograms, no matter which hole the transmitter was in, provided all other factors are equal. The method of data recording and processing did differ from those employed using the Swedish system, however. With the USGS system, the boreholes are logged with the probes moving at about 12 cm/s (25 ft/min) at constant depth offsets from one another. An exceptionally high-speed data acquisition system designed and built by the USGS (Wright and others, 1989) allowed averaging 512 waveforms for signal-to-noise improvement while recording the averaged data every 17 cm. Because half the data were used in producing the tomograms, the effective data interval was about 35 cm. Five different offsets were used. The maximum offset used was +/-10 m, so the steepest angle was about +/-38°.

The seismic equipment was developed and fabricated by scientists at the Lawrence Berkeley National Laboratory (LBL). The equipment consists of a seismic source, a receiver string, and a data-recording system. For the 1991 survey from which the displayed tomogram is derived, the seismic source consisted of a high-voltage, high-fidelity amplifier which delivers electrical pulses of 5 kV amplitude and 20 ms width through a coaxial cable to a downhole piezoelectric source. In this pulse mode, the generated seismic signal has a dominant frequency content in the 5 to 8 kHz range. For a seismic velocity of 5,000 m/s, the wavelength is approximately 1 m. Both the source and receiver stations were at 1-m intervals. The data-recording system consists of a computer with 16-bit analog-to-digital converter.

All three systems record the full waveform, so that any refinements in picking and processing could be applied to the original data in the future. All three systems also provide real-time computer-screen displays of the recorded waveforms so that the system operator can instantly detect gross system malfunction and have some assurance of the integrity of the recorded data without requiring playback or analysis.

One experimental factor should be mentioned that has been a problem for the radar systems, however. If the time base drifts, it will induce errors in the data. It is known that both the USGS and the ABEM systems sometimes have exhibited drift. For the 1992 field season, a new experimental procedure was used with the USGS system to allow detection, measurement, and correction for time-base drift, should it occur. The USGS data processing also includes a unique consistency test of the data quality (Olhoeft, 1988).

TOMOGRAMS AND FRACTURE PROJECTIONS AT THE FSE4-FSE1 WELL PAIR

Figure 3 is a side-by-side display of three velocity tomograms between well FSE4 (left side) and well FSE1 (right side). The gray scale renditions printed here are inferior in detail; color displays are commonly superior. Figure 3a shows a velocity tomogram produced from data acquired using the ABEM system. The tomogram was produced using proprietary ABEM software. The algorithm used by ABEM is of the conjugate gradient type. All of the possible raypaths were used in producing the ABEM tomogram. Because some of the rays that are produced by connecting every measurement station in well FSE4 to every station in well FSE1 are nearly vertical, the angular coverage is very good for this tomogram. Figure 3b shows a velocity tomogram produced from data recorded with the USGS system and processed with software written by the USGS (Olhoeft, 1988). The tomogram was produced using a variational filtered back-projection algorithm. Figure 3c was produced from data acquired with the LBL borehole seismic system. The manually picked first arrival time data were processed using an algebraic reconstruction technique (Peterson and others, 1985).

An attenuation tomogram produced with the ABEM system and software is shown in figure 4a. An attenuation tomogram produced with the USGS system and software is shown in figure 4b. The attenuation scales in figures 4a and 4b are not calibrated, but the relative values are sufficient for purposes of visual comparison. Figure 4c is produced by projecting fractures recorded with the acoustic televiewer from wells FSE4 and FSE1 (Paillet and others, 1987, Paillet and Kepucu, 1989, Paillet, 1991, Paillet, 1996). The fractures recorded in each well FSE4 and FSE1 are projected in the plane of the walls from FSE4 half way to FSE1 and similarly for the fractures recorded in well FSE1. The projections are subject to errors of a few degrees, and the projections and other evidence
indicate that few, if any, fractures project in a straight line from one well to the other and that the flow between the wells does not follow a single well-defined path. There are probably hydraulic connections between fractures; therefore, if one overlays the fracture projections on the tomograms with the idea of finding correlations with the tomograms, one should bear in mind that the evidence indicates that relatively few fractures can be projected very far in the FSE well field.

COMPARISONS OF THE TOMOGRAMS AND FRACTURE PROJECTIONS

All the tomograms begin at about 20 m depth, slightly below the bottom of the steel casing in both wells. When well FSE4 is pumped and the hydraulic transmissivities of various fractures are measured by the flowmeter, a small number of fractures dominate hydraulic flow. The high-transmissivity fractures are shown in figure 4c as heavy lines. The arrows along the sides of each tomogram indicate the location of those high-transmissivity fractures except for the one at a depth of about 18 m in well FSE 1. The slope of the arrows roughly indicates the dip of the water-producing fractures recorded with the acoustic televiewer and confirmed to be a water-producer by the flowmeter. Most (80 percent) of the water that enters well FSE4 when it is pumped flows through the fracture indicated by the upper arrow.

At well FSE4, the velocity lows in figures 3a and 3b seem to reflect a dense nest of fractures just above the upper of the two arrows (see fig. 4c). The seismic tomogram of figure 3c also show a response. At well FSE1, figure 3a shows a velocity low about 2 m above the indicated fracture location. Figure 3b shows a larger zone of relatively low velocity. In none of the tomograms can the flow paths between wells be defined with precision, though hints may be seen. It is possible that substantial flow even leaves the plane of the wells, a situation that cannot be determined by 2-dimensional tomography. Directional borehole radar, a capability of the ABEM system, might perhaps reveal whether such flow occurs. It is evident that the tomogram in figure 3a has been smoothed to a greater degree than the tomogram of Figure 3b. Some detail might have been lost in the process, although some might argue that the USGS data have not been smoothed enough. Near-horizontal features appear to be more sharply defined in figure 3b as a result of the eight times greater spatial density of data. On the other hand, figure 3a indicates some steep contours in the 50- to 70-m depth range, and the 80- to 100-m range. Such features are not evident in figure 3b. The limited angular coverage of the USGS data might be expected to produce tomograms that would distort or miss just such long, near-vertical features. A conclusion is that both high spatial data density and wide angular coverage are desirable. There are some differences among figures 3a, 3b, and 3c in the hydraulically important 39- to 47-m deep zone. Two minima in the velocity in figure 3a occur adjacent to the wells. In figure 3b, on the other hand, a minimum velocity is attained near the middle of the zone. Figure 3c shows velocity lows both along the boreholes and in the interior. If figures 3b and 3c are accurate in this respect, they could indicate probable flow paths. Finally, it should be noted that the appearance of visual shapes can sometimes be considerably altered by rescaling the color or gray-scale representation of the data without altering the underlying data in any way.

The gross structure of figures 4a and 4b is similar. Both show a closed area of relatively low attenuation at about the 30-m depth, rapidly grading to relatively high attenuation higher in the section. The USGS plot does not extend to a depth of 20 m, but the ABEM tomogram indicates relatively high attenuation in the upper right-hand corner that correlates with the projection of the water-producing fracture intersecting well FSE1 at a depth of about 18 m. Both tomograms also show a zone of relatively high attenuation at about the 40-m depth. The two patterns are remarkably similar in shape but appear to be offset from one another by about 3 m. This local attenuation high is several meters above the projection of the water-producing fracture in well FSE1. The ABEM tomogram has a distinctive boot-shaped area of moderate attenuation, with the toe of the boot pointing down and to the right and ending at about 70 m depth. There is a narrow strip adjacent to well FSE1 from about 47 m to the toe of the boot where the attenuation is low. In figure 4b, a zone of low attenuation is also seen, but the precise shape is somewhat different. Another zone of low attenuation is seen in the depth interval from about 75 to about 90 m in figure 4b with a corresponding area shown in figure 4a. The contours in the lower left-hand corner of figure 4a oriented down and to the right appear to correlate with fracture projections in the corresponding part of figure 4c, although, in other areas, correspondence to fracture projections is not clear.
CONCLUSIONS

The EM and seismic tomograms do correlate, though imperfectly, with each other and with some known fractures. Interpretations of tomograms for fracture mapping is made more difficult because tomograms map lithology as well as fractures. Detailed lithologic logs of wells FSE1 and FSE4 are not yet available, but it is known that the fractured rock in well FSE1, the rock is schist or granite, and, in well FSE4, the rock is pegmatite, granite, and schist. Granites, schists, and pegmatites can have overlapping ranges of electrical and elastic properties that govern the propagation of electromagnetic and seismic waves. It appears that, of the two EM tomograms, the ABEM tomograms are superior for detecting steeply dipping features, and the USGS tomograms are superior for detecting nearly horizontal features but would benefit from steeper angular coverage, which would not be difficult to obtain, although it would require some changes to the tomography-processing algorithm.

Higher resolution is desirable. In the rock observed in wells FSE1 and FSE4, the attenuation is low enough that it would be possible to use frequencies higher than 60 MHz (perhaps 120 MHz) for EM tomography. The trade-off is that, in using higher frequencies, the attenuation will increase; thus, in many cases, especially in widely spaced wells, there will not be sufficient signal to work with. This is true for either EM or seismic systems. Other possibilities include examination of the data to see whether diffractive tomography might be possible (Olhoeft, 1988) and emphasizing what happens to the high-frequency end of the amplitude spectrum (dispersion tomography) in reprocessing existing data (Wright and others, this proceedings).

There is much work yet to be done. Tomography has tended to be done in isolation with little or no reference to other borehole geophysics or lithology information. It is time to begin the task of data integration in the pursuit of improving our understanding of ground-water flow through fractured rock.

REFERENCES


Hydraulic Characteristics of Fractured Bedrock Underlying the FSE Well Field at the Mirror Lake Site, Grafton County, New Hampshire

By Paul A. Hsieh\textsuperscript{1} and Allen M. Shapiro\textsuperscript{2}

Abstract

At the Mirror Lake site in Grafton County, New Hampshire, 13 wells are drilled in a 120-m (meter) by 80-m area, known as the FSE well field, the characterize the hydraulic and transport properties of the underlying fractured bedrock. Borehole geophysical logs and downhole video camera images show that each well intersects 20 to 60 fractures within the upper 60 m of bedrock. However, single-well hydraulic tests show that only one to three fractures in each well are highly transmissive. Multiple-well hydraulic tests suggest that the few highly transmissive fractures connect with one another locally to form fracture clusters. These highly transmissive fracture clusters, in turn, connected to one another by fractures that are comparatively lower in transmissivity by several orders of magnitude. In such a fractured-bedrock setting, the response to a multiple-well hydraulic test is entirely different from the response in a homogeneous aquifer. These findings suggest that it is necessary to identify and characterize explicitly the highly transmissive fracture clusters in order to analyze multiple-well hydraulic tests at the FSE well field.

INTRODUCTION

Development and testing of field methods to determine the hydraulic and transport properties of fractured rocks are major objectives of a field study at the U.S. Geological Survey Toxic Substances Hydrology Program research site in the Mirror Lake

\begin{figure}
\centering
\includegraphics[width=\textwidth]{map}
\caption{Map showing arrangement of wells in the FSE well field.}
\end{figure}

\textsuperscript{1}U.S. Geological Survey, Menlo Park, Calif.
\textsuperscript{2}U.S. Geological Survey, Reston, Va.
BEDROCK AND FRACTURES AT THE FSE WELL FIELD

Overlain by approximately 20 m of glacial drift, the bedrock at the FSE well field consists of schist that is extensively intruded by granite and pegmatite. At a nearby road cut on highway I-93, the exposed bedrock shows a complex distribution of rock types (CC. Barton, U.S. Geological Survey, written commun., 1993). The granitic intrusions have the form of dikes, irregular pods, and anastomosing fingers, ranging from centimeters to tens of meters thick. The pegmatite intrusions have the form of dikes, centimeters to meters thick, cross cutting both the schist and the granite. Although basaltic dikes have been observed in the Mirror Lake area, they have not been encountered in wells drilled at the FSE well field.

Thirteen wells are drilled into bedrock at the FSE well field. Well construction begins with mud-rotary drilling through the glacial drift at the top 3 m of bedrock. A 15-cm inside-diameter (i.d.) steel casing is cemented in the drill hole. After the cement has hardened, drilling continues by air-percussion to create a 15-cm-diameter open hole to the desired depth in the bedrock. The only exception to this procedure was the construction of well FSE5, which was first cored as a 9-cm-diameter hole and then reamed to a diameter of 15 cm. Eight of the 13 wells in the FSE well field are 75 to 85 m deep. The shallowest well is 61 m deep; the deepest well is 229 m deep.

Rock types and fractures encountered in the wells are determined by examining drill cutting, viewing the borehole walls with a downhole video camera (C.D. Johnson, U.S. Geological survey, written commun., 1993), and detecting fractures with a borehole televiewer (Paillet, 1985; Paillet and Kapucu, 1989). The drill cuttings and video images show that the FSE wells penetrate variable thicknesses of schist, granite, and pegmatite. However, there is little to no apparent correlation between rock types in neighboring wells. This lack of correlation is consistent with the complex patterns of rock-type distribution on the I-93 road cut.

SINGLE-WELL HYDRAULIC TESTS

Borehole-televiewer logs show that each FSE well intersects 20 to 60 fractures within the upper 60 m of bedrock. Transmissivities of these fractures are determined by single-well hydraulic tests. These tests employ two inflatable packers to isolate a section of the well. Water is either injected or withdrawn from the test interval, and the flow rate and pressure change are recorded. By assuming steady, horizontal, radial flow, the transmissivity of the test interval is calculated by the Theim equation (as discussed by Bear, 1979). Because the intact rock is much less transmissive than the fractures, the computed transmissivity is attributed entirely to the fractures that intersect the test interval. If only one fracture intersects the test interval, the calculated transmissivity is the combined transmissivity of the fractures. Because of practical considerations, single-well hydraulic tests in the FJSE wells are conducted with 4.5-m-long test intervals. This means that fractures spaced less than 4.5 m apart are tested together as a group. Infractors sections of wells are not tested.

The distribution of fractures and their transmissivities in well FSE11, which is 85-m deep and is cased over the upper 25 m, are shown in figure 2.

Figure 2. (a) Vertical distribution of transmissivity determined from single-well hydraulic tests in well FSE11. Bar thickness indicates length of test interval. (b) Borehole televiewer log of well FSE11.
The borehole-televiewer log shows that the well intersects approximately 25 fractures below the casing. Because most of these fractures are tested in groups, it is not possible to determine the transmissivity of each fracture. Nevertheless, the test results shown in figure 2 clearly indicate that only a few fractures have a high transmissivity (greater than $10^{-5}$ m$^2$/s), whereas most of the fractures have a much lower transmissivity (less than $2 \times 10^{-8}$ m$^2$/s). Highly transmissive fractures are present at depths of 46 m and 80 to 85 m. By measuring borehole flow while pumping the open well, Paillet and others (1987) conclude that highly transmissive fractures are present at the same locations.

With the exception of well FSE7, which does not intersect any highly transmissive fractures, characteristics of fractures at all the wells in the FSE well field are similar to those at FSE11; that is, 20 to 60 fractures are observed in each well within the upper 60 m of bedrock. Of the fractures, only a few are highly transmissive. These observations suggest that the highly transmissive fractures could play an important role in controlling fluid flow in the FSE well field.

### MULTIPLE-WELL HYDRAULIC TESTS

The hydraulic connections between the highly transmissive fractures intersected by the FSE wells are investigated by multiple-well hydraulic tests. To set up a test, the highly transmissive fractures in each well are isolated from one another by installing packers in unfractured parts of the borehole. The packers divide each well into separate intervals, each interval continuing either (a) a single highly transmissive fracture, or (b) several highly transmissive fractures that are close to one another (that is, a few meters apart). In the latter case, the closely spaced fractures are assumed to be part of a well-connected fracture cluster, so there is no attempt to isolate these fractures from one another. Although each interval also contains fractures of comparatively low transmissivity, it is the highly transmissive fracture (or fracture cluster) that dominates the hydraulic head in the interval. Therefore, the hydraulic response observed in each interval represents the hydraulic response of the highly transmissive fracture in that interval.

During a multiple-well hydraulic test, water is pumped at a constant rate from one interval, and the hydraulic-head responses field setup described above, the this amounts to pumping from a highly transmissive fracture, and monitoring drawdown in all the other highly transmissive fractures. The hydraulic connection between these fractures are inferred from the response to pumping. For example, if two highly transmissive fractures are connected by other highly transmissive fractures in the bedrock, the drawdowns in the two fractures should be nearly identical. In contrast, if two highly transmissive fractures are not connected by other highly transmissive fractures in the bedrock, the drawdowns in the two fractures could be significantly different.

A hypothesized distribution of fractures in the vertical section between wells FSE1 and FSE6 is shown in figure 3. Results of multiple-well hydraulic tests suggest that the highly transmissive fractures intersected locally to form four fracture clusters, denoted by I to IV in figure 3. The fracture clusters are, in turn, connected to one another by fractures of comparatively lower transmissivity. Preliminary analysis of test data indicates that these fractures are several orders of magnitude less transmissive than the fractures that form clusters I to IV.

![Diagram showing hypothesized distribution of fractures in vertical section between wells FSE1 and FSE6. Four clusters of highly transmissive fractures occur within a network of less transmissive fractures.](image-url)
the drawdown at well FSE9, because drawdown must be greater than the pumped interval for converging flow to enter. Within fracture clusters I, II, IV, drawdown appears to be internally uniform. For example, at fracture cluster II, identical drawdowns are observed at wells FSE5, FSE4, and FSE1, located 57.9 m, 88.4 m, and 101.3 m respectively from well FSE6. This uniformity of drawdowns at different distances from the pumped well is direct evidence that the fractures in the cluster are in good hydraulic connection. The fact that the hydraulic heads in fracture clusters I, II, and IV respond to pumping from fracture cluster III, but the responses are quite different from one another, suggests that the four fracture clusters are connected to each other by fractures of comparatively lower transmissivity.

The drawdown responses described above is entirely different from the drawdown response in a homogeneous aquifer, in which the drawdown decreases progressively with increasing distance from the pumped well. At the FSE well field, the highly transmissive fracture clusters exert a strong control on the drawdown response during a multiple-well hydraulic test. This finding suggests that it is necessary to identify and characterize the highly transmissive fracture clusters explicitly in order to analyze the test response. Quantitative analysis of the test data is the focus of the ongoing work.

**SUMMARY AND CONCLUSIONS**

Results of single-well hydraulic tests at the FSE well field show that, of the 20 to 60 fractures intersected by each of the 13 wells, only one to three are highly transmissive. Results of multiple-well hydraulic tests suggest that these highly transmissive fractures are interconnected locally to form fracture clusters. These fracture clusters are, in turn, connected to each other by a network of fractures several orders of magnitude lower in transmissivity. In such a setting, the drawdown response to a multiple-well hydraulic test is entirely different from the drawdown response in a homogeneous aquifer. These findings suggest that it is necessary to identify and characterize the highly transmissive fracture clusters explicitly in order to analyze multiple-well hydraulic tests at the FSE well field.

**REFERENCES**


A New Method of Performing Controlled Injection of Traced Fluid in Fractured Crystalline Rock

By Allen M. Shapiro¹ and Paul A. Hsieh²

Abstract

A new method is presented for the controlled injection of traced fluids into permeable intervals in bedrock wells. Prior to the tracer injection, an inflatable packer is used to seal fractures in the injection interval, allowing downhole mixing of the tracer with borehole water. After a uniform mixture is achieved, the packer is deflated to inject the traced fluid into the fractures. The injection apparatus requires smooth borehole walls and no more than a few closely spaced permeable fractures in the injection interval. In this paper, operation of the equipment is presented for the instantaneous injection of a known volume of traced fluid into the formation. The equipment can also accommodate other injection procedures, such as the continuous injection of traced fluids into the formation.

INTRODUCTION

Controlled-tracer tests are conducted in subsurface terranes to identify formation properties such as effective porosity and dispersivity. These tracer tests are conducted under either hydraulically stressed or ambient-flow conditions by introducing a known mass of a tracer into the formation and monitoring its spatial distribution at several times or its temporal variation at one or more locations.

Regardless of the type of hydraulic conditions used to conduct the tracer test, the identification of formation properties requires a knowledge of the flow regime and a knowledge of the temporal or spatial distribution of the tracer concentration after it has been introduced into the formation. It is also crucial to have an explicit knowledge of the temporal variation of the tracer concentration as it is introduced into the formation. If the method of introducing the traced fluid into the formation is not well known, then the interpretation of the tracer test becomes ambiguous.

In this paper, a newly designed injection apparatus is presented for the controlled injection of traced fluids into permeable sections of bedrock wells in crystalline rock. The operation of this equipment permits the injection of a known volume and concentration of a traced fluid into the formation over a specific period of time. In particular, the application of this equipment to the instantaneous injection of a traced fluid into fractured rock is discussed.

EFFECT OF VARIABLE HYDRAULIC PROPERTIES ON THE INJECTION OF TRACED FLUIDS

The bedrock of the Mirror Lake watershed in the Hubbard Brook Experimental Forest in Grafton County, New Hampshire (fig. 1) has been a site for the development of field techniques and interpretive methods of characterizing fluid movement and chemical transport in fractured rock (Shapiro and Hsieh, 1991). The bedrock in the Mirror Lake watershed is a sillimanite-grade schist with extensive intrusions of granite and pegmatite, and lesser amounts of basalt. The variability in hydraulic conductivity, fracturing and rock type along the length of borehole H-l are shown in figure 2. The hydraulic conductivity was measured using single-hole, fluid-
injection test over 5-m-long intervals along the length of the borehole. Only intervals containing fractures were tested; the hydraulic conductivity of the unfractured rock matrix was assumed to be below the detection limit of the injection-test apparatus, which is approximately $10^{-10} \text{ m/s}$. The rock type was identified using a borehole television camera (C. D. Johnson, U.S. Geological Survey, written commun., 1992) and the location of fractures was determined from an acoustic televiewer log (F. L. Paillet, U.S. Geological Survey, written commun., 1992).

The fracturing and hydraulic conductivity shown in figure 2 are typical of boreholes in crystalline rock. The fractures are not uniformly spaced, and the hydraulic conductivity varies over 4 orders of magnitude with abrupt changes over relatively short distances. Not all of the fractured sections of the borehole have measurable hydraulic conductivity. In some instances, the injection rates were below the detection limit of the testing apparatus, and thus, a measurable hydraulic conductivity could not be assigned to the interval.

Because of the extreme variability in the hydraulic conductivity, the controlled injection of a traced fluid into the formation cannot be conducted in an open borehole. The volume and concentration of the traced fluid entering the formation at each of the permeable sections of the borehole can not be explicitly identified. Also, it would be difficult to quantify the concentration of the tracer residing in the

Figure 1. Location of Mirror Lake watershed in New Hampshire.
Figure 2. Hydraulic conductivity, acoustic televiewer and lithologic logs for borehole H-1 in the Mirror Lake watershed, Grafton County, New Hampshire.

borehole and then diffusing into the formation. Consequently, it is necessary to design a controlled environment for injecting traced fluid into bedrock formations for the purposes of conducting controlled-tracer tests.

A straddle-packer assembly is commonly used to isolate a permeable section of a bedrock well for hydraulic testing or the injection of traced fluids. A straddle-packer assembly consists of two packers, each with a flexible bladder that can be enlarged by
mechanical or pneumatic means to seal against the borehole wall. The interval between two packers is hydraulically isolated from the remainder of the borehole. A traced fluid can be injected into the straddled interval, and then the straddled interval can be flushed with tracer-free water. This procedure, however, does not guarantee that all of the traced fluid will be forced into the formation. Because of density differences between the ambient fluid and the traced fluid, or incomplete flushing in the straddled interval, some of the tracer can reside in the straddled section of the borehole and diffuse into the formation over time. This will affect the character of the temporal or spatial distribution of the tracer concentration in the formation and could result in erroneous interpretations of formation properties. Reducing the length of the straddled interval such that only the fracture is hydraulically isolated would eliminate this problem. However, it is difficult to reduce the distance between packers to less than 0.5 m, which could still cause problems in identifying the explicit temporal variation of the tracer concentration as it is introduced into the formation.

**NEW TRACER INJECTION METHOD**

To provide for the controlled injection of traced fluids into permeable sections of bedrock wells in crystalline rock, a new tracer injection system has been designed to seal off the permeable fractures intersecting the borehole between the straddle packers. The equipment is schematically depicted in Figure 3a. The equipment consists of 3 packers (labeled A, B, and C), and two valves controlling the "injection" and a "return" tubing.

The packers labeled A and C are inflated prior to the start of the hydraulic test to hydraulically isolate a section of the borehole where there is a permeable fracture (fig. 3b). Packer B is positioned so that it will block off the permeable fracture or fractures in the interval straddled by the top (A) and bottom (C) packers when it is inflated. Thus, relatively smooth borehole walls and only one or two closely spaced permeable fractures in the injection interval are required. These conditions are most likely to be encountered in crystalline rock.

Information on fracture location and hydraulic conductivity must be obtained prior to conducting the tracer test. For example, the location of fractures can be identified using a combination of borehole geophysical logging tools such as the acoustic televiewer and caliper logs (Paillet, 1991) and a borehole television camera. The permeable sections of the borehole can be identified by using a flow meter while pumping water from the open borehole to identify locations where fluid enters the borehole from the formation (Hess, 1986). More exact measurements of hydraulic conductivity can be made using injection tests, similar to those described in the previous section (the results of which are shown in fig. 2).

Prior to starting the tracer test, the middle packer is inflated to block off the permeable fracture in the straddled interval (fig. 3c). A tracer solution is then prepared at land surface. The concentration of this tracer solution should be sufficient to achieve the desired injection concentration when it is mixed with the volume of tracer-free water residing between packers A and C. The injection and return valves are opened, and the tracer solution is then pumped through the "injection" tubing, and it is circulated between the packers. The mixed water returns to the surface through the "return" tubing and to the fluid reservoir containing the tracer solution (fig. 3d). With the middle packer inflated, none of the tracer is introduced into the formation. The tracer solution is circulated until it is well mixed in the reservoir at land surface and in the volume between packers A and B, and B and C. Once this is achieved, the injection and return valves are closed, and the volume and concentration of the water in the reservoir at land surface is measured.

The injection of the traced fluid is started by deflating the middle packer and opening the injection valve. The tracer is pumped down the injection tube and is forced into the formation (fig. 3e). The injection of traced fluid into the formation is terminated by inflating the middle packer to block the permeable fractures in the straddled interval (fig. 3f). The volume of water remaining in the fluid reservoir at land surface is then measured to determine the volume of the traced fluid injected into the formation.

The tracer solution between packer A and B, and B and C is then flushed with tracer-free water. This is done to ensure that the tracer is not introduced into the formation accidentally during the test or once the test is completed. The flushing of the tracer is conducted by opening the injection and return valves and using tracer-free water to flush the straddled interval through the "injection" tubing. The water exiting from the "return" tubing is monitored until the background concentration is achieved.
Figure 3. (a) New straddle packer assembly used for the controlled injection of traced fluids. (b) Packers A and C inflated to isolate injection interval in bedrock well. (c) Packer B inflated to seal permeable fracture in the injection interval. (d) Injection and return valves opened and traced fluid is circulated to mix in volume between packers A and B, and B and C. (e) Packer B deflated and injection valve opened to inject traced fluid into permeable fracture. (f) Packer B inflated to terminate injection; injection and return valves opened and tracer-free water circulated to flush traced fluid between packers A and B, and B and C.
Figure 3. (a) New straddle packer assembly used for the controlled injection of traced fluids. (b) Packers A and C inflated to isolate injection interval in bedrock well. (c) Packer B inflated to seal permeable fracture in the injection interval. (d) Injection and return valves opened and traced fluid is circulated to mix in volume between packers A and B, and B and C. (e) Packer B deflated and injection valve opened to inject traced fluid into permeable fracture. (f) Packer B inflated to terminate injection; injection and return valves opened and tracer-free water circulated to flush traced fluid between packers A and B, and B and C—Continued.

SUMMARY

The interpretation of controlled tracer experiments in subsurface terranes requires a knowledge of the temporal variation in the concentration of the traced fluid as it is injected into the formation. Because of abrupt spatial changes in hydraulic properties in fractured rock, it is difficult to perform the controlled injection of traced fluid in open sections of bedrock wells. Density differences between the ambient fluid and the traced fluid, and the lack of adequate circulation of the traced fluid in the borehole usually results in a residual concentration in the borehole that diffuses into the formation.

A new method for the injection of traced fluid into permeable intervals in bedrock wells uses a string of three inflatable packers. This newly designed injection apparatus permits the controlled injection of traced fluids into fractures within a hydraulically isolated section of a borehole. Prior to the tracer injection, the middle packer is used to seal off the fractures in the injection interval, allowing downhole mixing of the tracer with borehole fluid. After a uniform mixture is achieved, the middle packer is deflated to allow injection of the traced fluid into the formation. The equipment requires smooth borehole walls and no more than a few closely spaced permeable fractures.

In this paper, operation of the new injection apparatus is presented for the instantaneous injection of a known volume of traced fluid into the formation. The equipment can also accommodate other injection procedures, such as the continuous injection of traced fluids into the formation.

REFERENCES


Field Instrumentation for Multilevel Monitoring of Hydraulic Head in Fractured Bedrock at the Mirror Lake Site, Grafton County, New Hampshire

By Paul A. Hsieh¹, Richard L. Perkins², and Donald O. Rosenberry³

Abstract

An adjustable and removable instrument, consisting of commercially available components, was developed for monitoring hydraulic heads at several depth intervals in bedrock wells. The intervals are isolated from each other by packers. Each interval is connected to an open pipe, so that the water level in the pipe equals the hydraulic head in the interval. The water levels are monitored by a potentiometer-float system and automatically recorded by a datalogger. The water levels are also measured manually by a water-level probe to check periodically the automatic measurements. The hydraulic-head monitoring instrument can be removed from the well to accommodate activities such as geophysical logging, water sample collection, or hydraulic testing. This instrumentation has been installed at 12 bedrock wells at the Mirror Lake site.

INTRODUCTION

Accurate measurement of hydraulic head is essential for monitoring fluid flow in the subsurface. In particular, a measurement of the vertical distribution of hydraulic head is needed to determine the vertical component of fluid flow. In shallow alluvial material, the vertical distribution of hydraulic head can be measured by installing a cluster of piezometers screened at different depths. In most bedrock environments, the cost of drilling and casing multiple wells to different depths is prohibitively high, so that the hydraulic heads at different depths must be measured in a single well. However, an open well can perturb the natural flow field by connecting highly permeable fracture zones that are unconnected in the absence of the well. Therefore, packers are generally needed to divide the well into separate intervals and to isolate the highly permeable fracture zones from one another. To complicate matters, the well could be needed for other purposes, such as collecting water samples, geophysical logging, and testing new instruments. Accordingly, any instrument installed in the well must be removable. This paper describes a removable instrument developed for multilevel monitoring of hydraulic heads in bedrock wells at the U.S. Geological Survey Toxic Substances Hydrology research site in the Mirror Lake area, Grafton County, New Hampshire.

DESIGN CRITERIA

To accommodate the many uses of a bedrock well, the hydraulic-head monitoring instrument is designed according to the following criteria: (1) The instrument had to divide the well into several intervals so that the hydraulic head in each interval could be measured separately. (2) Each interval had to be connected to an open pipe, so that the hydraulic head could be measured either manually with a water-level probe, or automatically with a potentiometer-float device or an electronic pressure transducer. The manual measurements would provide checks on the automatic measurements. (3) The instrument had to be removable so that the well can be used for purposes such as geophysical logging, water quality sampling, or hydraulic testing. Upon completion of work, the instrument would be reinstalled in the well. (4) The
The instrument had to be adjustable so that the monitored interval could be modified should the need arise. The instrument had to be made of components that are commercially available to minimize the need for specialized fabrication.

DESCRIPTION OF INSTRUMENT

Figure 1 is a schematic diagram showing the instrument set up for multilevel monitoring of hydraulic head in a bedrock well. The well is cased through the overburden and is left as an open hole below the casing. Two packers are suspended on 3-cm-inside-diameter (i.d.) steel pipes. When inflated with air, the rubber bladder of the packer swells and presses against the borehole wall, creating a pressure-tight seal. The two packers separate the well into three intervals: A, B, and C. The hydraulic head in each interval is a composite of the hydraulic heads in the transmissive fractures that intersect the interval. In many cases, the interval contains a single, highly transmissive fracture or fracture zone that dominates the hydraulic head in the interval.

Each interval is connected to a 5-cm i.d. pipe so that the water level in the pipe equals the hydraulic head in the interval. The 5-cm i.d. is needed to accommodate a potentiometer-float system for automatic water-level measurement. Hydraulic head in the bottom (C) interval is measured in the 5-cm i.d. steel pipe that is connected to the 3-cm i.d. steel pipe on which the packers are suspended. The hydraulic head in the middle (B) interval is measured in a 5-cm i.d. polyvinyl-chloride (PVC) pipe that is connected to the interval by means of a nylon tubing. The hydraulic head in the upper (A) interval is the water level in the well casing. This water level is also measured through a 5-cm i.d. PVC pipe to avoid tangling the float with tubing in the well. Not shown in figure 1 are the nylon tubing used to inflate the packers.

A potentiometer-float system (Rosenberry, 1990a) is used to measure water levels in the 5-cm i.d. pipes (fig. 2). The wire on which the float and counterweight are suspended is wrapped around the wheel of a potentiometer. As the water level changes, the float moves, turning the wheel and changing the electrical resistance of the potentiometer. This change in resistance is converted back to water level and recorded by a datalogger. Under controlled laboratory
conditions, this potentiometer-float system can detect a water level change of 0.1 cm. However, during long-term operation in the field, the wire may gradually slip against the potentiometer wheel, causing a larger error. A study by Rosenberry (1990b) shows that, during long-term operation, water levels are measured by a potentiometer-float system with an accuracy of ±1 cm.

In principle, the well can be divided into more than three intervals by installing more than two packers. In practice, the number of intervals is limited by the number of pipes that can fit inside the well casing. Because a minimum inside diameter of 5 cm is needed to accommodate the float, only three pipes can fit inside a 15-cm i.d. well casing. Reducing the pipe diameter allows additional intervals to be monitored, but requires the use of a smaller float, which lessens the sensitivity of the recorder to water-level changes. Accurate measurement of water-level change in a smaller diameter pipe may require the use of alternative water-level sensors such as electronic pressure transducers.

**INSTALLATION OF INSTRUMENT**

Before installing the hydraulic-head monitoring instrument, some preliminary information is needed to select appropriate locations for packer placement. In general, packers are placed between the highly transmissive fractures to isolate them from each other. These highly transmissive fractures can be identified by hydraulic testing with straddle packers, or by measurement of flow in borehole during pumping (Paillet and others, 1987). A packer should be placed where the borehole wall is smooth and unfractured to achieve a pressure-tight seal. A caliper log is extremely helpful for identifying locations where the borehole wall is rough or broken; such sections in the borehole should be avoided. Borehole-image logs, such as those made by borehole televiewers and video cameras, provide detailed information on fracture locations.

Once the packer placements are selected, the instrument can be installed in the well. In general, a well-servicing vehicle (work-over rig) or a tripod-winch assembly is needed to lower the packers and pipes into the well. The depth range of each interval can be easily adjusted by cutting the 3-cm i.d. steel pipes to the desired length. Installing the three 5-cm-diameter i.d. pipes requires special care, because all three pipes are lowered simultaneously into the well. The PVC pipes are affixed to the steel pipe by steel bands.

After the packers are lowered into position and are inflated, a platform is attached to the well head. The potentiometers are then mounted on the platform. The well-head installation, including the datalogger, is covered by an aluminum box, which provides shelter from rain and snow.

**MONITORING HYDRAULIC HEADS IN THE MIRROR LAKE AREA**

Monitoring hydraulic heads in fractured bedrock is part of an interdisciplinary study on fluid flow and chemical transport in fractured rocks at the U. S. Geological Survey Toxic Substances Hydrology research site in the Mirror Lake area in central New Hampshire (fig. 3). As discussed by Shapiro and Hsieh (1991), the objectives of this study are to develop monitoring and testing methods for characterizing ground-water flow and solute transport in bedrock, and to establish a site for long-term study. Although the Mirror Lake area is not contaminated, the techniques and understanding developed in this study are directly transferable to other fractured rock sites where ground water has been contaminated with chemical wastes.

As of early 1993, multilevel hydraulic-head monitoring instruments have been installed in 12 bedrock wells. Hydraulic heads are recorded automatically once every hours. Each well is inspected once a week to check that the instrument is working properly. Several packers tend to leak air and must be repressurized from time to time. During each visit, water levels are measured manually for comparison with the automatic measurements. As more experience is gained from this operation, the frequency of visit will decrease to approximately one visit per month.

Figure 4 illustrates the hydraulic heads recorded at well site FS3 during 1991. During this period, hydraulic heads were manually measured once a week. Interval A in the bedrock well extends from the bottom of casing (depth of 11.6 m) to a depth of 25.5 m below land surface. Interval B extends from a depth of 26.2 m to 59.2 m. Interval C extends from a depth of 59.9 m to the bottom of the well (depth of 196.6 m). In addition to the heads in the bedrock well, figure 4 also shows the heads in three nearby piezometers installed at depths of 4.3 m, 6.7 m, and 8.8 m in the glacial drift overlying the bedrock. The decrease of hydraulic head with depth suggests a downward component of flow from the glacial drift into the bedrock at this well site.
SUMMARY

An adjustable and removable instrument has been developed to monitor the hydraulic heads in packer-isolated intervals in a bedrock well. The hydraulic head in each interval can be monitored by measuring the water level in an open pipe connected to the interval. Because the pipes are open, automatic water-level measurements can be made using a potentiometer-float system. Periodic manual measurements using a water-level probe provide a check of the automatic measurements. The instrument can be removed from the well to accommodate activities such as geophysical logging, water-sample collection, and hydraulic testing. This instrumentation has been installed at 12 bedrock wells at the Mirror Lake site.

REFERENCES


Factors Affecting Recharge to Crystalline Rock in the Mirror Lake Area, Grafton County, New Hampshire

By Philip T. Harte¹ and Thomas C. Winter²

Abstract

The effects of local and regional-flow processes on recharge to crystalline rock are investigated by use of numerical, cross-sectional models of ground-water flow, comparison of vertical-head gradients between lower piezometers in drift and upper bedrock wells, and chemical mass-balance models of net differences in water chemistry. This paper describes factors that control recharge to crystalline rock in the Mirror Lake area. Four principal factors that affect bedrock-recharge patterns are (1) relief of land and bedrock surface above ground-water discharge areas, (2) lateral trends in bulk-rock horizontal hydraulic conductivity, (3) local topographic features, and (4) drift stratigraphy. Factors 1 and 2 control the regional distribution of bedrock recharge, whereas the local distribution of bedrock recharge is controlled by factors 3 and 4.

INTRODUCTION

The spatial distribution of bedrock recharge from overlying unconsolidated deposits is an important factor in delineating areas susceptible to the advective transport of contaminants. Crystalline-rock aquifers in many areas of the country that have been glaciated have few surface exposures. The low hydraulic conductivity of these aquifers can cause the water table to be shallow and to be present primarily in the overlying unconsolidated drift in humid environments. Few studies have evaluated the distribution of bedrock recharge from overlying drift, although Keeler and others (1988) have indicated that unconsolidated deposits can control rates of bedrock recharge.

This paper describes factors that affect bedrock recharge from overlying glacial drift. Two numerical, steady-state cross-sectional models of ground-water flow are used to evaluate recharge processes: (1) A model of a generalized hillside-valley system representative of New England and (2) A model of the Mirror Lake area. Results of the modeling experiments are compared to the distribution of vertical head between glacial drift and bedrock at 14 locations, and to the vertical distribution of ground-water chemistry at 2 locations (FS3 and FS1) in the Mirror Lake area (fig. 1).

FACTORS AFFECTING BEDROCK RECHARGE FOR HYPOTHETICAL SYSTEMS

The model of the hypothetical setting is patterned after the generalized characteristics of the physiography and hydrogeology encountered in the Mirror Lake area and elsewhere in the glaciated northeast United States (fig. 2). The geologic setting consists of fractured crystalline rock overlain by a largely continuous mantle of glacial till, which in turn is overlain in places by stratified drift. A detailed discussion of the setting, finite-difference model (McDonald and Harbaugh, 1988), model assumptions and boundaries, and sensitivity tests is given in Harte (1992). The bulk hydraulic properties of the fractured crystalline rock are viewed as an equivalent porous medium over the dimensions of the investigation.
Figure 1. Vertical-head gradients between lower drift and upper bedrock from bedrock well nests (a), and location of well nests and shallow rock boreholes in the Mirror Lake area, Grafton County, New Hampshire (b) (modified from U.S. Forest Service, written commun., 1956).
Conditions tested include hydraulic conductivity variations of the drift and bedrock, modification of physiographic characteristics such as slope, basin-aspect ratio, and small topographic irregularities on the uniformly sloping terrain. Distribution of vertical-flow rates (bedrock recharge and discharge) from the overlying drift are shown in figure 2 for selected conditions. Results presented include simulations of layered units consisting of homogenous and isotropic material (glacial drift and bedrock), homogeneous and isotropic drift and heterogeneous crystalline rock, and small topographic features superimposed onto the uniform sloping hillside. Results from the layered homogenous and isotropic units serve as the reference "base" case. For the "base" case, each hydrogeologic unit has a uniform horizontal hydraulic conductivity in the following descending relation: stratified drift > till > bedrock.

Results indicate that besides relief of the land and bedrock surface and the distribution of ground-water discharge areas (sinks), which are the primary controls on topographically driven flow systems, the predominant controls on distribution patterns of bedrock recharge are lateral trends in bulk-rock hydraulic conductivity (horizontal heterogeneity) and topography.
The curves shown in figure 2 illustrate the following features: (1) Maximum recharge and discharge occur at changes in water-table slope coincident with changes in land-surface slope, (2) relatively small topographic features can cause localized recharge and discharge patterns in a regional recharge or discharge zone, and (3) relatively small horizontal trends in bulk-rock hydraulic conductivity can result in large variations in recharge and discharge zones.

Lateral trends in bulk-rock horizontal hydraulic conductivity (horizontal heterogeneity) significantly affect the size of bedrock recharge areas. The bulk-rock hydraulic conductivity can vary as a result of spatial-distribution patterns in fracture density and connectivity. Variation in bulk-rock hydraulic conductivity of one order in magnitude results in a 50-percent variation in the size of the bedrock recharge area from that produced under base conditions. The two tests shown in figure 2 include increasing and decreasing the hydraulic-conductivity distribution with decreasing altitude. The change in hydraulic conductivity of one order of magnitude is similar to the inferred hydraulic-conductivity distribution implied by topographic variations in well yields (LeGrand, 1967, Sever, 1964, and Knopman and Hollyday, 1993). The ripple effect in the curves is caused by a step-like approximation to a linear trend in hydraulic conductivity. Decreasing hydraulic conductivity with decreasing altitude results in a small regional recharge area and a large regional discharge area. Conversely, increasing hydraulic conductivity with decreasing altitude results in a large regional recharge area and a small regional discharge area.

Small topographic features cause localized bedrock recharge in regional recharge and discharge zones because they cause inflections in the water-table slope. Although this concept is not new and has been reported by others (Toth, 1962, 1963; and Freeze and Witherspoon, 1966-68), the results indicate a high degree of head sensitivity to topography in low hydraulic-conductivity aquifers because the water table is generally shallow and is very similar to land surface. Bedrock is recharged under downward inflections in the water table corresponding to downward inflections in land surface. Bedrock discharges under upward inflections in the water table corresponding to upward inflections in land surface. If local topographic features are associated with variations in drift stratigraphy, these features can exert greater control over bedrock recharge patterns (Harte, 1992).

### FACTORS AFFECTING BEDROCK RECHARGE IN THE MIRROR LAKE AREA

Results of a numerical model of the cross-sectional, ground-water flow in the Mirror Lake area (fig. 3) show the importance of relief and local ground-water sinks on regional flow in bedrock. The results presented are the best-fit approximation (closest match) between simulated and observed heads and show two important features of this low hydraulic-conductivity aquifer. The first feature is the steep hydraulic gradient on the hillside and the shallow depth to the water table beneath the hilltop. The second is the strong control of local ground-water sinks (Mirror Lake) relative to regional ground-water sinks (Pemigewasset River). The flow system associated with Mirror Lake extends to nearly the full depth of the simulated ground-water system. The lake also receives a small amount of ground-water discharge from the eastern side, the side toward the regional ground-water sink.

The distribution of vertical-head gradients between lower drift and upper bedrock indicates that bedrock receives recharge across much of the upland adjacent to Mirror Lake (table 1 and fig. 1). Vertical-head gradients show a strong correlation with land-surface altitude (coefficient of determination is 0.75) and bedrock-surface altitude (coefficient of determination is 0.73).

Further comparison of vertical-head gradients between lower drift and upper bedrock indicates that discharge from bedrock is restricted to areas where the bedrock water-level-sample midpoint is less than 213 m above mean sea level (table 1), which is the lake level for Mirror Lake. The sample midpoint is the average vertical distance of the open bedrock interval and is the reference point for the bedrock water level. The strong relation between altitude of bedrock midpoint and bedrock recharge and discharge indicates that the flow system is significantly affected by relief relative to local ground-water sinks.

The predominance of bedrock recharge determined from vertical-head gradients along the lower third of the hillside indicates the possible occurrence of lateral trends in bulk-rock hydraulic conductivity. An increase in horizontal hydraulic conductivity with a decrease in altitude, such that low hydraulic-conductivity rocks underlie hilltops and high hydraulic-conductivity rocks underlie valleys, would produce the observed distribution pattern of bedrock recharge. Otherwise, the lower hillside would be a bedrock discharge area.
Figure 3. Location of line of (a) regional section and the Mirror Lake watershed, and (b) geohydrologic section showing lines of equal head and generalized pathlines from best-fit model.
Table 1. Vertical-head gradients in the Mirror Lake area, Grafton County, New Hampshire
[m, meters; m/m, meters per meters; minus sign indicates upward flow; --, no data]

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<th>Altitude of average water level (m above sea level)</th>
<th>Midpoint of open interval (m above sea level)</th>
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<td>T1</td>
<td>Drift</td>
<td>T1-A</td>
<td>229.62</td>
<td>228.05</td>
<td>227.50</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>Upper bedrock</td>
<td>T1-A</td>
<td>229.15</td>
<td>224.95</td>
<td>210.28</td>
<td>0.18000</td>
</tr>
<tr>
<td>FSE</td>
<td>Upper drift</td>
<td>FSE6-WT</td>
<td>242.99</td>
<td>238.51</td>
<td>238.11</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>Lower drift</td>
<td>FSE6-59</td>
<td>243.03</td>
<td>237.49</td>
<td>224.52</td>
<td>0.07480</td>
</tr>
<tr>
<td></td>
<td>Upper bedrock&lt;sup&gt;1&lt;/sup&gt;</td>
<td>FSE6-A</td>
<td>242.90</td>
<td>235.79</td>
<td>214.45</td>
<td>0.18088</td>
</tr>
<tr>
<td></td>
<td>Upper drift</td>
<td>FSE2-WT</td>
<td>240.98</td>
<td>235.80</td>
<td>234.67</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>Lower drift</td>
<td>FSE2-43</td>
<td>241.01</td>
<td>234.20</td>
<td>226.92</td>
<td>0.20709</td>
</tr>
<tr>
<td></td>
<td>Upper bedrock&lt;sup&gt;1&lt;/sup&gt;</td>
<td>FSE2-A</td>
<td>241.07</td>
<td>234.07</td>
<td>208.29</td>
<td>0.01358</td>
</tr>
<tr>
<td>CO</td>
<td>Upper drift</td>
<td>CO1-WT</td>
<td>217.78</td>
<td>217.78</td>
<td>214.15</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>Lower drift</td>
<td>CO1-18</td>
<td>217.91</td>
<td>217.91</td>
<td>211.75</td>
<td>0.00380</td>
</tr>
<tr>
<td></td>
<td>Upper bedrock</td>
<td>CO1-A</td>
<td>217.97</td>
<td>216.23</td>
<td>191.41</td>
<td>-0.01874</td>
</tr>
<tr>
<td></td>
<td>Upper bedrock</td>
<td>CO2-A</td>
<td>216.88</td>
<td>215.51</td>
<td>196.66</td>
<td>-0.02242</td>
</tr>
<tr>
<td>K1</td>
<td>Upper drift</td>
<td>K1-WT</td>
<td>215.37</td>
<td>212.84</td>
<td>211.99</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>Lower drift</td>
<td>K1-39</td>
<td>215.38</td>
<td>211.91</td>
<td>205.59</td>
<td>0.14524</td>
</tr>
<tr>
<td></td>
<td>Bedrock</td>
<td>K1</td>
<td>215.41</td>
<td>212.67</td>
<td>186.11</td>
<td>-0.03897</td>
</tr>
<tr>
<td>K2</td>
<td>Upper drift</td>
<td>K2-WT</td>
<td>215.76</td>
<td>210.37</td>
<td>208.61</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>Lower drift</td>
<td>K2-41</td>
<td>215.62</td>
<td>210.46</td>
<td>202.51</td>
<td>-0.01552</td>
</tr>
<tr>
<td></td>
<td>Bedrock</td>
<td>K2</td>
<td>215.19</td>
<td>211.31</td>
<td>182.09</td>
<td>-0.05415</td>
</tr>
<tr>
<td>K3</td>
<td>Upper drift</td>
<td>K3-WT</td>
<td>208.16</td>
<td>206.09</td>
<td>201.75</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>Lower drift</td>
<td>K3-61</td>
<td>207.83</td>
<td>204.65</td>
<td>189.53</td>
<td>0.11798</td>
</tr>
<tr>
<td></td>
<td>Bedrock</td>
<td>K3</td>
<td>207.16</td>
<td>206.44</td>
<td>169.07</td>
<td>-0.08723</td>
</tr>
</tbody>
</table>

<sup>1</sup>Estimated water level

The distribution of piezometer nests, which are located predominantly on hillside terraces, can contribute to the observed distribution of bedrock recharge. The stratigraphy of the drift in most terraces, including FS3 and FS3C, FSl, and FSE (fig. 1) consists of an upper, relatively permeable sandy layer (kame terrace deposit) overlying a lower, less permeable till layer. These conditions can produce local areas of bedrock recharge within a regional discharge zone because the water table is commonly elevated in the terrace as a result of infiltration of precipitation recharge through the sand that exceeds vertical flow through the underlying till (Harte, 1992).
Local topography can also affect bedrock recharge and discharge. Upward and downward inflections of the land and corresponding inflections in the water table can produce discharge and recharge. Bedrock recharge occurs at piezometer nests TR1, T1, FS3C, and FS2 (fig. 1) near a downward inflection in the slope of the land. Bedrock discharge occurs at piezometer nest TR2 near an upward inflection in the slope of the land (fig. 1). However, local topographic features cannot fully explain the observed distribution of bedrock recharge and discharge. For example, bedrock recharge occurs at piezometer nest R1 although it is near an upward inflection in slope of the land (fig. 1). However, the local topography produces divergence of vertical flow in the lower drift (table 1).

Upward flow occurs from lower to upper drift and downward flow occurs from the lower drift to upper bedrock.

**BEDROCK RECHARGE PATTERNS BASED ON WATER CHEMISTRY**

Model experiments indicate two possible bedrock-recharge patterns resulting from either regional or local control. Solute and isotopic chemistry of the water are used here to define which of these processes is most probable.

Two possible vertical-flow patterns resulting from regional and local controls on bedrock recharge are shown for part of a hillside between two adjacent terraces (fig. 4). Regional control on bedrock recharge, caused by lateral trends in bulk-rock hydraulic conductivity, results in bedrock recharge over the entire area (fig. 4a). Local control on bedrock recharge, caused by local topography or drift stratigraphy, results in the formation of local-flow cells between adjacent terraces (fig. 4b). Vertical-head gradients between lower drift and upper bedrock indicate bedrock recharge occurs under each terrace (table 1). Linear interpolation of heads between terraces indicates that bedrock recharge also might occur between terraces. However, the effects of either flow pattern on water chemistry at the FS1 terrace should result in distinct chemical signatures, which would help verify the primary bedrock-recharge process.

Mass-balance and fractionation water-chemistry processes are modeled to assess the evolution of water chemistry as a result of various flowpaths. The interactive computer code "NETPATH" (Plummer and others, 1991) is used to interpret net geochemical mass-balance reactions between initial and final water along a possible hydrologic flowpath. The principle behind mass-balance modeling of the evolution of water chemistry is to reconstitute final water chemistry through source/sink reactions with initial water chemistry.

The conceptual chemical model used here is based on water-chemistry reactions in silicate terrains (Garrels, 1967; Bricker and others; 1968). These reactions indicate that the dominant effect on water chemistry in silicate terrain is reaction of carbon-dioxide enriched water, from contact with the atmosphere (open system), with plagioclase feldspars and biotite to form clay minerals. The initial and final concentrations of elements involved in these reactions,
sodium, silica, calcium, potassium, and carbon, are used to constrain model reactions between proposed evolutionary waters. An additional constraint is imposed on the system by modeling carbon-13 concentrations with calcite and carbon dioxide inputs from the atmosphere (open system) and/or organic decay. Calcite has been observed in petrographic rock analysis of crystalline rock from the Mirror Lake area (W.W. Wood, U.S. Geological Survey, oral commun., 1993). The ground-water-chemistry data used in the analysis includes major cations and anions and the carbon-13 isotope (W.W. Wood, U.S. Geological Survey, written commun., 1992) from lower drift and upper bedrock wells at FS3 and FS1 (table 2).

The evolutionary paths of water chemistry evaluated are shown in table 3. The initial and final water chemistry is tested by use of the conceptual chemical model to determine the feasibility of flowpaths. The feasibility of flowpath existence is determined by checking whether final waters can be reconstituted from the specified reactions discussed in the conceptual chemical model and the initial water input. The flowpaths evaluated include vertical flow between lower drift and upper bedrock at each terrace and lateral flow between terraces.

Net differences in water chemistry between lower drift and upper bedrock under the FS3 and FS1 terraces satisfy the constraints of the specified conceptual chemical model and vertical-head gradient, and indicate that bedrock recharge occurs under each terrace. Satisfactory reaction results are obtained that produce clay minerals from dissolution of feldpars and biotite. Upper bedrock cores collected from beneath each terrace reveal the presence of clay minerals. The modeled chemical reactions also indicate calcite dissolution under the FS3 and FS1 terraces and an increase in the heavier carbon isotope, carbon-13, which agrees with carbon-13 data. The thermodynamic potential of these waters supports calcite dissolution.

Net differences in water chemistry between terraces fails to support the presence of a local-flow cell connecting terrace FS3 with FS1. Final waters in the lower drift at FS1 could not be reconstituted from a mixing input of initial drift and bedrock waters from FS3. If a local-flow cell connected the two terraces, bedrock discharge would occur on the uphill side of the FS1 terrace and waters at FS1 lower drift should reflect a component of bedrock-derived waters, if the relative amount of flow in the till and bedrock are similar.

The results of the water-chemistry analysis of lower drift and upper bedrock waters underlying the FS3 and FS1 terraces indicate that upper bedrock waters are primarily derived from vertical flow through lower drift, although some lateral flow in bedrock between terraces might occur. The analysis of water chemistry suggests bedrock recharge occurs over the entire area between terraces. This interpretation is consistent with available head data.

### Table 2. Chemistry of selected lower drift and upper bedrock ground water from the Mirror Lake area, Grafton County, New Hampshire

<table>
<thead>
<tr>
<th>Chemical constituent</th>
<th>FS3-22 (Lower drift)</th>
<th>FS3-A (Upper bedrock)</th>
<th>FS1-35 (Lower drift)</th>
<th>FS1-A (Upper bedrock)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6.9</td>
<td>7.1</td>
<td>7.7</td>
<td>7.2</td>
</tr>
<tr>
<td>Eh (volts)</td>
<td>.227</td>
<td>-.025</td>
<td>.43</td>
<td>.154</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>10.0</td>
<td>8.5</td>
<td>8.5</td>
<td>9.5</td>
</tr>
<tr>
<td>Alkalinity (mg/L as HCO₃⁻)</td>
<td>26.8</td>
<td>61</td>
<td>39</td>
<td>39</td>
</tr>
<tr>
<td>Calcium as Ca (mg/L)</td>
<td>4.7</td>
<td>11</td>
<td>9.1</td>
<td>5.9</td>
</tr>
<tr>
<td>Magnesium as Mg (mg/L)</td>
<td>1.2</td>
<td>3.9</td>
<td>1.6</td>
<td>1.8</td>
</tr>
<tr>
<td>Sodium as Na (mg/L)</td>
<td>3.6</td>
<td>4.6</td>
<td>3.6</td>
<td>4.4</td>
</tr>
<tr>
<td>Potassium as K (mg/L)</td>
<td>1.6</td>
<td>3.7</td>
<td>1.7</td>
<td>1.6</td>
</tr>
<tr>
<td>Iron as Fe (μg/L)</td>
<td>5,300</td>
<td>1,000</td>
<td>13</td>
<td>3,900</td>
</tr>
<tr>
<td>Strontium as Sr (μg/L)</td>
<td>30</td>
<td>93</td>
<td>37</td>
<td>48</td>
</tr>
<tr>
<td>Chloride as Cl (mg/L)</td>
<td>.5</td>
<td>1.2</td>
<td>.6</td>
<td>.5</td>
</tr>
<tr>
<td>Sulfate as SO₄ (mg/L)</td>
<td>14</td>
<td>8.6</td>
<td>6.6</td>
<td>12</td>
</tr>
<tr>
<td>Fluoride as F (mg/L)</td>
<td>.12</td>
<td>.20</td>
<td>.28</td>
<td>.33</td>
</tr>
<tr>
<td>Bromine as Br (mg/L)</td>
<td>&lt;.01</td>
<td>.06</td>
<td>&lt;.01</td>
<td>&lt;.01</td>
</tr>
<tr>
<td>Nitrate as NO₃ (mg/L)</td>
<td>&lt;.01</td>
<td>--</td>
<td>.07</td>
<td>&lt;.01</td>
</tr>
<tr>
<td>Phosphate, ortho dissolved as P0₄ (mg/L)</td>
<td>&lt;.01</td>
<td>--</td>
<td>&lt;.01</td>
<td>&lt;.01</td>
</tr>
<tr>
<td>Silicate as SiO₂ (mg/L)</td>
<td>22</td>
<td>29</td>
<td>21</td>
<td>21</td>
</tr>
<tr>
<td>Carbon-13 as δ¹³C % relative to VPDB</td>
<td>-24.40</td>
<td>-12.65</td>
<td>-19.80</td>
<td>-17.10</td>
</tr>
</tbody>
</table>

The results of the water-chemistry analysis of lower drift and upper bedrock waters underlying the FS3 and FS1 terraces indicate that upper bedrock waters are primarily derived from vertical flow through lower drift, although some lateral flow in bedrock between terraces might occur. The analysis of water chemistry suggests bedrock recharge occurs over the entire area between terraces. This interpretation is consistent with available head data.
Table 3. Summary of flowpaths evaluated by use of chemical-reaction modeling to test the presence of a local-flow cell between FS3 and FS1 terrace, in the Mirror Lake area, Grafton County, New Hampshire

<table>
<thead>
<tr>
<th>Initial waters</th>
<th>Final waters</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>FS3-22 (Lower drift)</td>
<td>FS3-A (Upper bedrock)</td>
<td>Chemistry indicates evolution of waters; therefore, does not disprove flowpath. System closed to CO₂.</td>
</tr>
<tr>
<td>FS1-35 (Lower drift)</td>
<td>FS1-A (Upper bedrock)</td>
<td>Chemistry indicates evolution of waters; therefore, does not disprove flowpath. System closed to CO₂.</td>
</tr>
<tr>
<td>FS3-22 (Lower drift)</td>
<td>FS3-35 (Lower drift)</td>
<td>Chemistry indicates evolutionary waters; therefore, does not disprove flowpath. Works for open system to atmospheric input of CO₂ or fermentation reaction.</td>
</tr>
<tr>
<td>FS3-A (Upper bedrock)</td>
<td>FS1-A (Upper bedrock)</td>
<td>Chemistry indicates nonevolutionary waters; therefore, flowpath is unlikely.</td>
</tr>
<tr>
<td>FS3-22 (Lower drift)</td>
<td>FS3-A (Upper bedrock)</td>
<td>Chemistry indicates evolutionary waters from FS3-22 but not from FS3-A; therefore, strong influence of lateral flow in bedrock is unlikely. Need open system of CO₂ or fermentation reaction for evolution of FS3-22 waters to FS1-A waters.</td>
</tr>
<tr>
<td>FS1-35 (Lower drift)</td>
<td>FS3-A (Upper bedrock)</td>
<td>Chemistry indicates evolutionary waters primarily from FS1-35 (86 percent) and small amount from FS3-A (14 percent); therefore, vertical flowpath is not disproved with some lateral flow. Works for closed system.</td>
</tr>
<tr>
<td>FS3-22 (Lower drift)</td>
<td>FS1-35 (Lower drift)</td>
<td>Chemistry indicates non-evolutionary waters; therefore, flowpath is unlikely.</td>
</tr>
</tbody>
</table>

CONCLUSIONS

The predominant controls on distribution of recharge to crystalline rock in a mountainous New England setting are (1) relief of land and bedrock surface above ground-water sinks, (2) lateral trends in horizontal hydraulic conductivity in bedrock, (3) local topographic features, and (4) drift stratigraphy. Regional distribution of bedrock recharge is controlled by factors 1 and 2. Local distribution of bedrock recharge is controlled by factors 3 and 4.

The distribution of bedrock recharge in the Mirror Lake area is controlled primarily by relief of land and bedrock surface above ground-water sinks and lateral trends in horizontal hydraulic conductivity. The predominant distribution of vertical-head gradients indicate that bedrock recharge occurs throughout the lower parts of the hillside. The large area of bedrock recharge covering the low parts of the hillside probably results from lateral trends in bulk-rock horizontal hydraulic conductivity where the least permeable rocks underlie hilltops and the most permeable rocks underlie low-lying areas. Bedrock recharge appears to be less affected by local topographic features and drift stratigraphy than by lateral trends in bulk-rock horizontal hydraulic conductivity.

REFERENCES CITED


Concentrations of Chlorofluorocarbons and Other Gases in Ground Water at Mirror Lake, New Hampshire

By Eurybiades Busenberg and L. Niel Plummer

Abstract

The concentrations of chlorofluorocarbons (CFC's) were measured in samples of ground water from 51 different depth intervals in wells completed in the low-permeability glacial till and fractured crystalline rocks at Mirror Lake. The CFC concentrations were used to model water-recharge ages. The ground-water ages generally increased with depth from land surface and were consistent with the reconstructed tritium ($^3$H) concentrations. A 6°C water-recharge temperature was obtained from the nitrogen (N$_2$) to argon (Ar) ratios from the wells completed in the glacial till. The dissolved N$_2$, Ar, and helium concentrations generally increased with depth from land surface. Excess air in ground water ranges from about 0 to 19 cubic centimeters per liter in some deep wells. In addition to the excess air, some wells contain significant amounts of excess N$_2$. Enrichment in the concentrations of sulfate, calcium, and magnesium were present in some ground waters with CFC-recharge ages of 1963 to 1973.

INTRODUCTION

Flow of ground water through fractured rocks is difficult to characterize because of the complexity of the fracture network, the extreme variability in permeability and hydraulic properties of the bedrock, and difficulty of predicting the direction of fluid flow. Fractured-rock systems have the potential to transport fluids rapidly over large distances in a few highly permeable fractures. The age of the ground water can be a valuable tool in determining flow velocities, determining the hydraulic conductivities, and evaluating the direction of flow in such systems.

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The Mirror Lake watershed area is approximately 85 ha and is located at the eastern end of the Hubbard Brook Experimental Forest in Grafton County in central New Hampshire. A map of the area and the location of wells are given in Shapiro and others (1996). The precipitation and stream-water chemistry has been extensively studied for more than 20 years (Likens and others, 1977; 1985; Driscoll and others, 1989). The hydrogeologic setting has been described by Winters (1984). At Mirror Lake, the ground water is present in two distinct units—the overburden and the crystalline bedrock. The overburden consists largely of low-permeability glacial tills that store most of the ground water. The crystalline rocks have a network of fractures through which regional flow is thought to occur. Water samples collected from wells completed in the overburden and from discrete intervals in wells completed in crystalline rocks were used to determine CFC concentrations and water ages. Dichlorodifluoromethane (CFC-12), trichlorofluoromethane (CFC-11), and trichlorotrifluoroethane (CFC-113) are the most useful CFC's (Busenberg and Plummer, 1992; Busenberg and others, 1993) for dating recent recharge. Plummer and others (1993) compare and contrast the utility of the CFC's with that of tritium/helium ($^3$H/$^3$He) (Tolstikhin and Kamensky, 1969), and krypton-85 ($^{85}$Kr) (Rosanski and Florkowski, 1979) for dating young ground water.

This paper presents a summary of the results of CFC-dating of ground water at Mirror Lake for water samples collected in 1991 and 1992. A total of more than 290 ground-water samples were analyzed for concentrations of CFC-11 and CFC-12. In addition to concentrations of CFC-11 and CFC-12, concentrations of CFC-113 in the 1992 samples were also determined. In addition, concentrations of dissolved nitrogen (N$_2$), argon (Ar), carbon dioxide (CO$_2$), and methane (CH$_4$) in the ground waters were measured.
CONCENTRATIONS OF DISSOLVED GASES IN GROUND WATERS

Concentrations of \( \text{N}_2 \), \( \text{Ar} \), \( \text{CO}_2 \), and \( \text{CH}_4 \) were measured in 26 ground-water samples collected at Mirror Lake. Concentrations of \( \text{N}_2 \) and \( \text{Ar} \) generally increased with depth as shown in figure 1A and table 1. The partial pressure of \( \text{N}_2 \) in many ground waters exceeded 1 atmosphere, and many deep waters were observed to degas when pumped to the surface; this degassing may have affected the results slightly. The composition of sample 10 (table 1) was substantially modified by an air leak, and the concentrations of \( \text{N}_2 \) and \( \text{Ar} \) in sample 45 (table 1) are uncertain because of analytical problems.

The \( \text{N}_2 \) and \( \text{Ar} \) concentrations are shown in figure 1B. The water-recharge temperature of the sample on the diagram can be obtained by following a diagonal line (parallel to the temperature lines) from the sample to the recharge-water-temperature axis. The excess-air content of the sample can be obtained by following a diagonal line (parallel to the excess-air lines) from the sample to the excess-air axis. Possible trends in the evolution of dissolved gases in a ground water are shown in the lower right-hand corner of figure 1B. Presence of radiogenic \( \text{Ar} \) will shift the sample composition (filled circle) vertically as shown. Bacterial reduction of the solute nitrate to \( \text{N}_2 \) gas will shift the dissolved-gas composition horizontally. Addition of excess air will shift the composition diagonally. The slope of the line is determined by the \( \text{N}_2 \) to \( \text{Ar} \) ratio in air. In addition to the recharge-water temperature, these diagrams provide valuable information on the recharge mechanism of the ground waters (Mazor and Verhagen, 1983, 1984).

Ground waters from wells completed in the overburden (table 2) plot near the water in equilibrium with air (WEA) or zero-excess-air line and give a gas-recharge temperature of about 6°C. Most ground water from the crystalline fractured rocks deviate from the WEA line, and the deviation is generally greater for waters obtained from the deeper packed intervals. The waters contain far more \( \text{N}_2 \) than could be derived from the reduction of nitrates because the nitrate concentrations in precipitation (Likens and others, 1977), and in the shallow ground water are very low (W.W. Wood and A.M. Shapiro, U.S. Geological Survey, written commun., 1993). The high \( \text{Ar} \) concentrations in some waters could not have been derived from the radioactive decay of potassium-40 in the tens of years since recharge. The ground waters could have been contaminated with compressed air because modern air was used to power the pumps; however, mass-balance calculations on CFC’s indicate that the excess air was not modern air. The excess \( \text{N}_2 \) and \( \text{Ar} \) cannot be entirely attributed to excess air because the ratios of these two gases in many ground waters are not those found in air. A possible source of excess \( \text{N}_2 \) may have been leakage from \( \text{N}_2 \)-filled packers. Even though no pressure drops were observed in the packers, this source of \( \text{N}_2 \) cannot be totally dismissed at this time. In addition, high concentrations of \( \text{He} \) were observed in deep ground waters (Drenkard and others, 1996), and this \( \text{He} \) could not have been introduced by the sampling.

Similar high \( \text{N}_2 \) and \( \text{Ar} \) concentrations were observed in ground waters from fractured rocks from Yosemite National Park in California (J.W. Bochers, U.S. Geological Survey, written commun., 1992), and high \( \text{N}_2 \) and possible \( \text{He} \) concentrations have been reported in waters from boreholes in crystalline rocks in Sweden (Hermansson and others, 1991). It is conceivable that the dissolved-gas compositions may have been modified by the addition of gases released from the crystalline rock. \( \text{N}_2 \), \( \text{Ar} \), and \( \text{He} \) are trapped in minerals and fluid inclusions of igneous and metamorphic origin (Roedder, 1972, p. J132-J162 and table 2). Deep circulating ground waters may be discharging at Mirror Lake. Mixing of these waters with modern recharge could be producing the anomalous dissolved-gas compositions. Additional dissolved-gas samples were collected in 1993, and the isotopic composition of the \( \text{N}_2 \) indicates that the ground-water samples were not contaminated with compressed air or with \( \text{N}_2 \) from the \( \text{N}_2 \)-filled packers (J.K. Bohlke, U.S. Geological Survey, oral commun., 1993). The 1993 results have not been fully evaluated.

THE CHLOROFLUOROCARBON-DATING METHOD

CFC’s are stable synthetic organic compounds that were first manufactured in the 1930’s and are entirely of anthropogenic origin (Lovelock, 1971). Detectable concentrations of CFC-12, CFC-11, CFC-113 are present in post-1940, 1945, and 1973 waters, respectively. A detailed description of the method and the special procedures that are required to collect and analyze water samples containing CFC’s are described in detail elsewhere (Busenberg and Plummer, 1992;
Nitrogen concentration in equilibrium with air at 6°C

DEPTH BELOW LAND SURFACE, IN FEET

NITROGEN CONCENTRATION, IN MILLIGRAMS PER LITER

Figure 1A. Concentrations of nitrogen as a function of depth, at Mirror Lake, New Hampshire. The wells completed in the glacial tills are of less than 65 feet deep. The composition of sample 10 was modified by an air leak into the sampler. Symbols are well identifiers and entries above symbols are sample numbers, listed in table 2.

Figure 1B. Dissolved nitrogen and argon concentrations in ground water collected at Mirror Lake. (Concentrations were normalized to a total pressure of 1 atmosphere.)

Busenberg and others, 1993). The concentrations of CFC’s in water vary as a function of the atmospheric partial pressures are calculated from the measured CFC concentrations in ground water from the ground-water recharge temperature by means of Henry’s Law; the partial pressures were then compared to those depicted in the reconstructed atmospheric growth curves of Busenberg and others (1993) and Elkins and others (1993).

Uncertainties in CFC-modeled ages result from (1) differences in concentrations of CFC’s in the unsaturated-zone air at the water table from the northern-hemisphere continental troposphere (such differences occur in semiarid regions with thick unsaturated zones; Weeks and others, 1982); (2) elevated atmospheric CFC concentrations in industrial or large urban areas (Hester and others, 1974); (3) introduction of CFC’s from the pump, tubing, or other sampling equipment; (4) contamination of ground water form sewage or other sources (Busenberg and Plummer, 1992; Dunkle and others, 1993); (5) removal of CFC’s by sorption onto lignite or other organic matter in the aquifer (Ciccioli and others, 1980; Russell and Thompson, 1983); or (6) removal of CFC’s by biogenic degradation in highly anaerobic environments (CFC-11 degrades more rapidly than CFC-12; Lovley and Woodward, 1992).

Recharge dates of water containing CFC’s were calculated using a recharge temperature of 6°C; results of the calculations are given in table 2. The most reliable dates were obtained from use of CFC-12 concentrations. About 35 percent of waters (table 2) were contaminated with CFC-11 and CFC-113, and their measured concentrations exceeded the concentrations that would be in equilibrium with the 1992 atmosphere. The principle source of contamination appears to have been the plastic water-discharge tubing connecting the pump to the CFC-sampling apparatus, and the rubber packers. Rubber and plastic tubing sorbs significant amounts of CFC-11 and CFC-113, which are slowly released into the ground water during sampling (Reynolds and others, 1990).

GROUND-WATER AGES AT MIRROR LAKE

The volume-weighted concentrations of $^3$H in the recharge waters were calculated from the reconstructed $^3$H concentrations (R.L. Michel, U.S. Geological Survey, written commun., 1993) and the Mirror Lake precipitation data (U.S. Forest Service, written commun., 1993), and then were decayed to the year 1992 (fig. 2A). The model-CFC-12 concentrations in water at the recharge temperature of 6°C are also shown in figure 2A. The CFC-12 recharge dates of ground waters as a function of their $^3$H content are given in table 1 and figure 2B. CFC-12 recharge dates refer to the time since the recharge water was isolated from the unsaturated-zone atmosphere, and are not necessarily the dates of precipitation. The dashed horizontal line shows the estimated $^3$H concentrations in the recharge calculated by the model for Mirror Lake; these concentrations are the average of the $^3$H concentrations of two snow samples collected in 1991.
Table 1. Concentration of gases and excess air and nitrogen in ground water from Mirror Lake, New Hampshire.

[Concentrations of gases are in milligrams per liter, and excess gases in cubic centimeters per liter. N₂, nitrogen; Ar, argon; CO₂, carbon dioxide; CH₄, methane; ft, feet]

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Well name and depth interval</th>
<th>Average depth (ft)</th>
<th>Measured concentrations</th>
<th>Excess gases</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CO-1 104-114 ft</td>
<td>109.0</td>
<td>21.81 0.9364 0.0 2.4 0.07</td>
<td>0.00 0.00</td>
</tr>
<tr>
<td>2</td>
<td>CO-1 420-430 ft</td>
<td>425.0</td>
<td>27.37 0.9231 0.1 2.7 0.00</td>
<td>6.77 0.00</td>
</tr>
<tr>
<td>7</td>
<td>FS1-17 ft</td>
<td>17.0</td>
<td>19.82 0.7527 0.2 3.2 0.28</td>
<td>0.15 0.00</td>
</tr>
<tr>
<td>8</td>
<td>FS1-25 ft</td>
<td>25.0</td>
<td>20.05 0.7529 0.2 3.0 0.00</td>
<td>0.35 0.00</td>
</tr>
<tr>
<td>9</td>
<td>FS1-35 ft</td>
<td>35.0</td>
<td>22.98 0.8257 3.2 0.00 0.00</td>
<td>2.85 0.00</td>
</tr>
<tr>
<td>10</td>
<td>FS1 121-136 ft</td>
<td>128.5</td>
<td>35.63 1.0923 3.2 9.4 0.00</td>
<td>15.00 0.00</td>
</tr>
<tr>
<td>11</td>
<td>FS1 309-324 ft</td>
<td>316.5</td>
<td>23.18 0.8219 4.225 0.00</td>
<td>3.45 0.00</td>
</tr>
<tr>
<td>12</td>
<td>FS1 348-363 ft</td>
<td>355.5</td>
<td>24.78 0.8258 2.856 0.1</td>
<td>6.45 0.00</td>
</tr>
<tr>
<td>13</td>
<td>FS2 134-149.3 ft</td>
<td>141.7</td>
<td>24.99 0.8422 0.1 17.2 0.24</td>
<td>3.48 0.00</td>
</tr>
<tr>
<td>14</td>
<td>FS3 C-24 ft</td>
<td>24.0</td>
<td>21.69 0.7604 7.1 25.8 0.18</td>
<td>3.35 0.00</td>
</tr>
<tr>
<td>17</td>
<td>FS3 C-29 ft</td>
<td>29.0</td>
<td>18.57 0.7869 0.1 18.6 0.09</td>
<td>0.00 0.00</td>
</tr>
<tr>
<td>18</td>
<td>FS3 60-75.1 ft</td>
<td>67.6</td>
<td>24.16 0.8625 0.0 6.0 0.00</td>
<td>3.46 0.00</td>
</tr>
<tr>
<td>19</td>
<td>FS3 294-309.1 ft</td>
<td>301.6</td>
<td>27.04 0.7830 0.0 5.2 0.00</td>
<td>2.10 5.70</td>
</tr>
<tr>
<td>27</td>
<td>H1 107-122 ft</td>
<td>114.5</td>
<td>22.64 0.8262 1.1 21.0 0.00</td>
<td>2.13 0.00</td>
</tr>
<tr>
<td>28</td>
<td>H1 178-193 ft</td>
<td>185.5</td>
<td>22.82 0.7315 1.4 29.0 0.06</td>
<td>0.00 3.20</td>
</tr>
<tr>
<td>33</td>
<td>Rl-35 ft</td>
<td>35.0</td>
<td>19.54 0.7561 10.1 7.4 0.00</td>
<td>0.00 0.00</td>
</tr>
<tr>
<td>34</td>
<td>Rl-55 ft</td>
<td>55.0</td>
<td>22.31 0.8271 2.0 0.00 0.00</td>
<td>1.44 0.00</td>
</tr>
<tr>
<td>39</td>
<td>Tl 57-72 ft</td>
<td>64.5</td>
<td>22.62 0.7896 2.102 0.00</td>
<td>3.88 0.00</td>
</tr>
<tr>
<td>43</td>
<td>TR1 170-190 ft</td>
<td>180.0</td>
<td>24.10 0.7534 1.9 0.9 0.01</td>
<td>0.00 4.50</td>
</tr>
<tr>
<td>44</td>
<td>TR1 271-299.9 ft</td>
<td>265.5</td>
<td>28.17 0.8042 0.0 1.4 0.09</td>
<td>2.95 3.80</td>
</tr>
<tr>
<td>45</td>
<td>TR1 298.6-327.4 ft</td>
<td>313.0</td>
<td>28.50 0.7879 0.0 2.3 0.00</td>
<td>3.15 6.50</td>
</tr>
<tr>
<td>46</td>
<td>TR1 390-397.8 ft</td>
<td>393.9</td>
<td>27.60 0.8100 0.0 1.4 0.02</td>
<td>3.75 4.70</td>
</tr>
<tr>
<td>47</td>
<td>TR1 482-489.8 ft</td>
<td>455.9</td>
<td>38.03 0.8224 0.0 1.4 0.00</td>
<td>6.80 12.80</td>
</tr>
<tr>
<td>48</td>
<td>TR2 151-170.1 ft</td>
<td>160.6</td>
<td>25.14 0.7975 0.0 1.9 0.00</td>
<td>3.00 2.85</td>
</tr>
<tr>
<td>49</td>
<td>TR2 270-289.1 ft</td>
<td>279.6</td>
<td>34.00 0.9453 0.0 5.8 0.00</td>
<td>13.20 2.95</td>
</tr>
<tr>
<td>50</td>
<td>TR2 426-445.1 ft</td>
<td>435.6</td>
<td>42.19 1.0355 0.0 6.5 0.00</td>
<td>19.00 6.10</td>
</tr>
</tbody>
</table>

(W.W. Wood and R.L. Michel, U.S. Geological Survey, oral commun., 1993). The measured ³H concentrations in ground water from shallow overburden wells are significantly lower than the estimated ³H concentrations in modern recharge. Several reasons may explain the discrepancy between the observed ³H and estimated ³H concentrations in the recharge water. The estimated ³H concentrations in recharge may be too high if the recharge occurs in the summer months when ³H concentrations in precipitation are lower compared to the concentrations during winter and spring, if the recharge water takes several years to reach the water table, or if the water sampled in the overburden wells consisted of a mixture of recent recharge with pre-1940's water discharged from the fractured bedrock. It is unlikely that significant recharge occurs during the summer months because of the high evapotranspiration (Likens and others, 1977). Recharge may take several years to reach the water table because the glacial till has low permeability at some locations; however, the overburden is highly heterogeneous and rapid recharge may occur at other locations.

Note that 35 TU was the highest measured ³H concentration in the ground waters; this concentration is one order of magnitude lower than the ³H concentration modeled at the 1963-bomb peak (figure 2A). Also note that the ³H peak in figure 2B does not correspond to the 1963-bomb ³H peak. Both of these results suggest that the samples are mixtures of waters of different ages. The observed mixing or dispersion of these waters may be natural or may represent an artifact of sampling. The concentrations of CFC’s and ³H are the volume-weighted average of the mixtures. The apparent age of the mixed waters depends on the proportions as well as the concentrations of the components in the mixture. The input function of the tracers (figure 2A) will significantly affect the volume-weighted concentration of the mixture. The CFC-12 apparent age will be slightly younger than the volume-
Table 2. Calculated chlorofluorocarbon water-recharge dates, tritium concentrations, pumping rates, field observations, and dissolved gases in ground water from Mirror Lake, New Hampshire

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Well name and depth interval</th>
<th>Oldest CFC-12-based date</th>
<th>Oldest CFC-11-based date</th>
<th>Oldest CFC-13-based date</th>
<th>Tritium on CFC-11-based date</th>
<th>Pumping rate</th>
<th>Field observations</th>
<th>Excess dissolved gases</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 CO-1 104-114 ft</td>
<td>1967.0</td>
<td>1964.0</td>
<td>&lt;1973</td>
<td>15.60</td>
<td>1.80</td>
<td>Ar</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 CO-1 162-175 ft</td>
<td>1955.0</td>
<td>1953.0</td>
<td>&lt;1973</td>
<td>4.80</td>
<td>3.20</td>
<td>Ar</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 CO-3 28-40 ft</td>
<td>Modern 1964.0</td>
<td>Cont.</td>
<td>13.80</td>
<td>1.60</td>
<td>...</td>
<td>...</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4 CO-3 78-102 ft</td>
<td>1966.5</td>
<td>1974.5</td>
<td>1981</td>
<td>10.30</td>
<td>5.10</td>
<td>...</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 CO-3 140-156 ft</td>
<td>1965.0</td>
<td>1975.0</td>
<td>1981</td>
<td>10.30</td>
<td>5.10</td>
<td>...</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6 CO-4 92-98.8 ft</td>
<td>1972.5</td>
<td>1970.5</td>
<td>1979</td>
<td>17.20</td>
<td>3.60</td>
<td>A</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FS-1 17 ft</td>
<td>Modern Cont.</td>
<td>...</td>
<td>11.80</td>
<td>0.80</td>
<td>O</td>
<td>Normal</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8 FS-1 25 ft</td>
<td>1985.0</td>
<td>Cont.</td>
<td>15.60</td>
<td>0.80</td>
<td>O, PP, Cu, pH 11</td>
<td>Normal</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9 FS-1 35 ft</td>
<td>1975.5</td>
<td>Cont.</td>
<td>...</td>
<td>31.50</td>
<td>10</td>
<td>O, PP, Cu, pH 6.5</td>
<td>Air</td>
<td></td>
</tr>
<tr>
<td>10 FS-1 172-186 ft</td>
<td>1987.0</td>
<td>Cont.</td>
<td>20.20</td>
<td>5.50</td>
<td>...</td>
<td>Air leak</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11 FS-1 309-324 ft</td>
<td>&lt;1940.0</td>
<td>1963.5</td>
<td>...</td>
<td>0.3</td>
<td>50</td>
<td>...</td>
<td>Air</td>
<td></td>
</tr>
<tr>
<td>12 FS-1 348-363 ft</td>
<td>&lt;1940.0</td>
<td>1963.5</td>
<td>1977</td>
<td>0.5</td>
<td>1.20</td>
<td>...</td>
<td>Air</td>
<td></td>
</tr>
<tr>
<td>13 FS-1 234-149.3 ft</td>
<td>1974.0</td>
<td>1987.3</td>
<td>1975</td>
<td>0.7</td>
<td>2.8</td>
<td>D</td>
<td>...</td>
<td></td>
</tr>
<tr>
<td>14 FS-2 236-251.3 ft</td>
<td>1967.0</td>
<td>1975.0</td>
<td>1979</td>
<td>0.4</td>
<td>4.5</td>
<td>D</td>
<td>...</td>
<td></td>
</tr>
<tr>
<td>15 FS-1 236-369.9 ft</td>
<td>1966.0</td>
<td>1968.0</td>
<td>1974</td>
<td>0.2</td>
<td>4.0</td>
<td>...</td>
<td>...</td>
<td></td>
</tr>
<tr>
<td>16 FS-1 232-234-24 ft</td>
<td>1926.0</td>
<td>Modern 12.90</td>
<td>...</td>
<td>O, Around casing</td>
<td>Air</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17 FS-3 25-29 ft</td>
<td>1989.5</td>
<td>1992.5</td>
<td>1989</td>
<td>12.60</td>
<td>0.5</td>
<td>O</td>
<td>Ar</td>
<td></td>
</tr>
<tr>
<td>18 FS-3 360-75.1 ft</td>
<td>1960.0</td>
<td>1969.0</td>
<td>Cont.</td>
<td>11.10</td>
<td>5.40</td>
<td>A</td>
<td>...</td>
<td></td>
</tr>
<tr>
<td>19 FS-3 294-309 ft</td>
<td>1950.0</td>
<td>Cont.</td>
<td>2.84</td>
<td>1.20</td>
<td>...</td>
<td>...</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20 FS-3 365-360 ft</td>
<td>1955.0</td>
<td>Cont.</td>
<td>2.10</td>
<td>5.40</td>
<td>...</td>
<td>...</td>
<td></td>
<td></td>
</tr>
<tr>
<td>21 FS-3 350-349 ft</td>
<td>1957.0</td>
<td>Cont.</td>
<td>2.48</td>
<td>4.00</td>
<td>...</td>
<td>...</td>
<td></td>
<td></td>
</tr>
<tr>
<td>22 FS-3 32-30-32 ft</td>
<td>1967.0</td>
<td>Cont.</td>
<td>14.30</td>
<td>...</td>
<td>O</td>
<td>...</td>
<td></td>
<td></td>
</tr>
<tr>
<td>23 FS-3 41-43 ft</td>
<td>1975.0</td>
<td>Cont.</td>
<td>21.00</td>
<td>...</td>
<td>O</td>
<td>...</td>
<td></td>
<td></td>
</tr>
<tr>
<td>24 FS-4 438-445 ft</td>
<td>&lt;1940.0</td>
<td>1973.0</td>
<td>1981</td>
<td>29</td>
<td>...</td>
<td>...</td>
<td></td>
<td></td>
</tr>
<tr>
<td>25 FS-5 106-115 ft</td>
<td>1955.0</td>
<td>1963.5</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td></td>
<td></td>
</tr>
<tr>
<td>26 FS-4 93-145 ft</td>
<td>1955.0</td>
<td>1953.5</td>
<td>1955</td>
<td>...</td>
<td>...</td>
<td>Variable</td>
<td>...</td>
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</tr>
<tr>
<td>27 FS-4 93-149 ft</td>
<td>1955.0</td>
<td>1953.5</td>
<td>1975</td>
<td>...</td>
<td>...</td>
<td>Variable</td>
<td>...</td>
<td></td>
</tr>
<tr>
<td>28 FS-4 104-140 ft</td>
<td>1955.0</td>
<td>1953.5</td>
<td>1975</td>
<td>...</td>
<td>...</td>
<td>Variable</td>
<td>...</td>
<td></td>
</tr>
<tr>
<td>29 FS-4 105-115 ft</td>
<td>1955.0</td>
<td>1953.5</td>
<td>1975</td>
<td>...</td>
<td>...</td>
<td>Variable</td>
<td>...</td>
<td></td>
</tr>
<tr>
<td>30 FS-4 125-135 ft</td>
<td>1955.0</td>
<td>1953.5</td>
<td>1975</td>
<td>...</td>
<td>...</td>
<td>Variable</td>
<td>...</td>
<td></td>
</tr>
<tr>
<td>31 FS-4 180-185 ft</td>
<td>1955.0</td>
<td>1953.5</td>
<td>1975</td>
<td>...</td>
<td>...</td>
<td>Variable</td>
<td>...</td>
<td></td>
</tr>
<tr>
<td>32 FS-4 190-195 ft</td>
<td>1955.0</td>
<td>1953.5</td>
<td>1975</td>
<td>...</td>
<td>...</td>
<td>Variable</td>
<td>...</td>
<td></td>
</tr>
<tr>
<td>33 FS-4 200-210 ft</td>
<td>1955.0</td>
<td>1953.5</td>
<td>1975</td>
<td>...</td>
<td>...</td>
<td>Variable</td>
<td>...</td>
<td></td>
</tr>
<tr>
<td>34 FS-4 215-220 ft</td>
<td>1955.0</td>
<td>1953.5</td>
<td>1975</td>
<td>...</td>
<td>...</td>
<td>Variable</td>
<td>...</td>
<td></td>
</tr>
<tr>
<td>35 FS-4 230-235 ft</td>
<td>1955.0</td>
<td>1953.5</td>
<td>1975</td>
<td>...</td>
<td>...</td>
<td>Variable</td>
<td>...</td>
<td></td>
</tr>
<tr>
<td>36 FS-4 240-245 ft</td>
<td>1955.0</td>
<td>1953.5</td>
<td>1975</td>
<td>...</td>
<td>...</td>
<td>Variable</td>
<td>...</td>
<td></td>
</tr>
<tr>
<td>37 FS-4 245-250 ft</td>
<td>1955.0</td>
<td>1953.5</td>
<td>1975</td>
<td>...</td>
<td>...</td>
<td>Variable</td>
<td>...</td>
<td></td>
</tr>
<tr>
<td>38 FS-4 251-255 ft</td>
<td>1955.0</td>
<td>1953.5</td>
<td>1975</td>
<td>...</td>
<td>...</td>
<td>Variable</td>
<td>...</td>
<td></td>
</tr>
<tr>
<td>39 FS-4 260-265 ft</td>
<td>1955.0</td>
<td>1953.5</td>
<td>1975</td>
<td>...</td>
<td>...</td>
<td>Variable</td>
<td>...</td>
<td></td>
</tr>
<tr>
<td>40 FS-4 270-275 ft</td>
<td>1955.0</td>
<td>1953.5</td>
<td>1975</td>
<td>...</td>
<td>...</td>
<td>Variable</td>
<td>...</td>
<td></td>
</tr>
</tbody>
</table>

weighted average age of the sample; however, any mixture that contains a small amount of bomb-peak water will have high $^3$H concentrations. The mixing of waters may partly account for the apparent shift of the $^3$H peak in figure 2B.

Figure 2B shows that samples 13, 14, 15, 38, and 41 (open circles) have essentially no $^3$H and must be older than their apparent CFC-12 ages. Indeed, samples 40 and 41 have significantly older CFC-11 and CFC-113 ages. Samples 13 and 14 have virtually no $^3$H and were almost certainly contaminated with CFC-11 and, possibly, with CFC-12 during sampling.

**CALCIUM, MAGNESIUM, AND SULFATE CONCENTRATIONS**

The concentrations of calcium (Ca), magnesium (Mg), and sulfate (SO$_4$) in the ground waters are shown as a function of the CFC-12 date of recharge in figure 3A. Also shown is the U.S. Environmental Protection Agency’s (1988) estimates of sulphur dioxide (SO$_2$) emissions for the northeastern United States, as well as the SO$_2$ emissions normalized to the amount of precipitation at Mirror Lake. The normalized SO$_2$ concentrations were obtained by solving the equation $E_f(P/P_{max})$, where E and P are the annual SO$_2$
emissions and precipitation, respectively. The subscripts i and max represent the i\textsuperscript{th} year and maximum amount observed, respectively. The data in figure 3 indicate that there is correlation among the Ca, Mg, and SO\textsubscript{4} concentrations in ground water, atmospheric SO\textsubscript{2} emissions, and the amount of precipitation. The high concentrations of SO\textsubscript{4} are present in ground water with CFC-dates of 1963 to 1973. CFC-model recharge dates are consistent with high emissions of SO\textsubscript{2}, and lower-than-normal rainfall. The results of Driscoll and others (1989) imply that the SO\textsubscript{4} and cation concentrations in precipitation peaked at approximately this time at Mirror Lake. No chemical data for precipitation at Mirror Lake are available prior to 1963.

**CONCLUSIONS**

Results from this study show that CFC's can be used to date ground waters from fractured rocks. Tritium, chemical, and hydrological information were useful in evaluating the CFC dates.

The CFC and \(^{3}H\) results indicate that considerable mixing of waters can occur as a result of sampling and also naturally in fractured-rock aquifers, resulting in a shifting of CFC-based ages to a slightly younger age than suggested by \(^{3}H\) concentrations. CFC-12 recharge dates refer to the time since the recharge water was isolated from the unsaturated-zone atmosphere and are not necessarily the age of the precipitation. The precipitation may take several years to reach the water table because of the low permeability of the glacial till overburden at some locations.

An average recharge temperature of 6°C was determined from the dissolved gas concentrations in ground water from wells in overburden. Anomalous concentrations of dissolved N\textsubscript{2} and Ar were found in ground water from the fractured crystalline rocks, and the dissolved gas concentrations in water increased with depth at Mirror Lake.

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Figure 3A. Relation of concentrations of magnesium, calcium, and sulfate in ground water to year of recharge based on chlorofluorocarbon-12 concentrations in ground water. Entries above symbols are sample numbers, listed in table 2.

Figure 3B. Amount of precipitation at Mirror Lake, estimates of sulfur dioxide emissions for the northeastern United States, and the sulfur dioxide emissions normalized to the precipitation at Mirror Lake.


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Helium Isotope Analysis and Tritium-Helium Age Dating in the Mirror Lake Basin, Grafton County, New Hampshire

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Abstract

Ground-water samples from the U. S. Geological Survey's Mirror Lake fractured bedrock site in New Hampshire were analyzed for tritium ($^3$H) and its decay product helium-3 ($^3$He) as well as for helium-4 ($^4$He) and neon (Ne). Parallel measurements of the radioactive mother/daughter pair $^3$H/$^3$He can be used to determine a ground-water age -- that is, the time elapsed since the water last equilibrated with the atmosphere. Preconditions for precise calculations by this method are separation of the tritiogenic $^3$He signal from other He components dissolved in water (atmospheric, nucleogenic and mantle $^3$He) by use of $^4$He and Ne data. This separation technique is complicated for samples analyzed from the Mirror Lake site because of a large helium excess with an estimated $^3$He/$^4$He ratio of about $1.65 \times 10^{-6}$. Water analysis from shallow wells yield reliable $^3$H/$^3$He-based ages, but the error in the age calculation increases with depth because of an increase in excess He and the related errors in the associated corrections. Possible origins of the excess He are discussed, and mixing of waters (young, tritium and $^3$He-enriched with old, $^4$He-enriched) as an apparent source is ruled out. He isotope measurements of crushed rock samples indicate that the source of excess He is not the local bedrock. On the basis of the observed increase in $^3$H/$^3$He age and presence of excess He with depth, the potential of the $^4$He concentration as an additional proxy age-dating tool is explored.

INTRODUCTION

An important concept for estimation of regional hydraulic properties beyond the space scale of borehole tests is knowledge of the travel time or 'age' of a water sample--that is, the time since last equilibration with the atmosphere. Three methods are used for ground-water age dating in the range of several months to several decades: the ratio of $^3$H to $^3$He concentrations (Tolstikhin and Kamensky, 1969; Torgersen and others, 1978), chlorofluorocarbon (CFC) concentrations (Busenberg and Plummer, 1991, 1992), and krypton-85 ($^{85}$Kr) decay (Smethie and others, 1992). The $^3$H/$^3$He technique works well in porous media (Poreda and others, 1988; Schlosser and others, 1988, 1989; Solomon and Sudicky, 1991) and is less vulnerable to local anthropogenic contamination than CFC dating. The $^3$H/$^3$He method has not been used extensively to study fractured-bedrock aquifers, although in principle it should be equally applicable. Age dating based on a combination of the CFC, $^{85}$Kr, and $^3$H/$^3$He methods has the potential to detect water mixing and, under favorable circumstances, even mixing rates. In addition, the He concentration can be used together with other geochemical tracers as a tool to determine general paths of ground-water flow. This paper describes the preliminary results of $^3$H/$^3$He dating and He isotope investigations in the well-characterized bedrock environment of the Mirror Lake watershed, New Hampshire. This investigation is part of the U.S. Geological Survey Toxic Substances Hydrology Program and was partially funded by the NATO and the 'Deutscher Akademischer Austausch Dienst'.

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SAMPLE COLLECTION AND MEASUREMENTS

Water samples for He-isotope and $^3$H analysis were collected with those for other geochemical analyses (for details see Shapiro and others, 1996). For $^3$H, 1 L of water was collected in glass bottles and analyzed by low-level gas counting after electrolytic enrichment. Water samples for He isotope analysis were collected in pinch-off copper tubes (3/8-in. i. d., about 80 cm long) carrying about 40 g of water. A flow-control valve was used to prevent degassing during sampling.

The dissolved gases were extracted from water samples using a vacuum extraction system and transferred into flame-sealed glass ampoules. He isotope concentrations were measured by a dedicated mass spectrometer after separation of water vapor, neon (Ne) and other gases. Ne was measured in a quadrupole mass spectrometer. Typical precision of the $^3$He/$^4$He ratio analysis is about ±1 to 2 percent. $^4$He in ground-water samples is measured routinely with a precision of ±1 to 3 percent. Because of the high helium concentrations, most of the gas samples had to be split before injection into the mass spectrometer; this had significant impact on the overall precision of the measurements of samples with high He excess.

$^3$H/$^3$He-DATING METHOD

The $^3$H/$^3$He-age-dating technique is based on the radioactive decay of atmospheric $^3$H that enters ground-water during recharge and the accumulation with time of its daughter product $^3$He. The age ($\tau$) can be calculated from the equation

$$\tau = \frac{T_{1/2}}{\ln(2)} \ln (1 + \frac{\text{He}_{\text{tri}}}{\text{He}})$$

where: $T_{1/2}$ = half life of $^3$H (12.43 years)

$[\text{He}_{\text{tri}}]$ = $^3$He concentration due to $^3$H decay

$[\text{He}]$ = $^3$He concentration corrected to the day of sampling

Although the $^3$H content in a sample can be measured directly, not all $^3$He ($^3$He$_{\text{tot}}$) in a water sample is of tritiogenic origin (Torgersen and others, 1978). In addition, there is an air saturation component, $^3$He$_{\text{sat}}$, depending on the recharge temperature, as well as possible supersaturation caused by the dissolution of air bubbles ($^4$He$_{\text{air}}$) during recharge. Occasionally, non-atmospheric $^3$He and $^4$He sources, $^3$He$_{\text{exc}}$ and $^4$He$_{\text{exc}}$, are observed.

$$^3\text{He}_{\text{tot}} = ^3\text{He}_{\text{sat}} + ^3\text{He}_{\text{air}} + ^3\text{He}_{\text{exc}} + ^3\text{He}_{\text{tri}}.$$ 

The air-related $^3$He contribution and the corresponding $^4$He$_{\text{air}}$ fraction, with the isotopic ratio of 1.384x10$^{-6}$, can be calculated as long as the recharge temperature and the Ne content are known:

$$^4\text{Ne}_{\text{tot}} = ^4\text{Ne}_{\text{sat}} + ^4\text{Ne}_{\text{air}}$$

$$^4\text{He}_{\text{tot}} = ^4\text{He}_{\text{sat}} + ^4\text{He}_{\text{air}} + ^4\text{He}_{\text{exc}}$$

$$^4\text{He}_{\text{air}} = (\text{He}/\text{Ne})_{\text{air}} \times (^4\text{Ne}_{\text{tot}} - ^4\text{Ne}_{\text{sat}})$$

$$^3\text{He}_{\text{air}} = 1.384 \times 10^{-6} \times (\text{He}/\text{Ne})_{\text{air}} \times (^4\text{Ne}_{\text{tot}} - ^4\text{Ne}_{\text{sat}})$$

where $^4\text{Ne}_{\text{tot}}$, $^4\text{Ne}_{\text{sat}}$, and $^4\text{Ne}_{\text{air}}$ are defined as above for He and the He/Ne ratio of air is 0.288 (for further details, see Schlosser and others, 1989).

Because $^3$H decay does not produce $^4$He, the difference between the measured $^4$He content and the calculated $^4$He$_{\text{air}}$ plus $^4$He$_{\text{sat}}$ yields the $^4$He fraction derived from in situ He sources ($^4$He$_{\text{exc}}$). If the $^3$He/$^4$He ratio of that additional source can be determined, the $^3$He contribution of the source can be calculated. The difference between the measured $^3$He and calculated $^3$He$_{\text{air}}$ plus $^3$He$_{\text{exc}}$ is the tritiogenic $^3$He fraction (for further details see Torgersen and others, 1978, and Schlosser and others, 1989):

$$^3\text{He}_{\text{tri}} = ^3\text{He}_{\text{tot}} - (^3\text{He}/^4\text{He})_{\text{air}} \times (^3\text{He}_{\text{sat}} + (\text{He}/\text{Ne})_{\text{air}} \times (^4\text{Ne}_{\text{tot}} - ^4\text{Ne}_{\text{sat}}))$$

RESULTS AND DISCUSSION

The results of the water-sample analyses are listed in table 1. Most of the samples have Ne concentrations within a factor of two of saturation and, therefore, a relatively small additional air component. On the other hand, a significant number of samples contain excess He that must have been added to the water in situ. For the Mirror Lake Basin ground-water samples, the measured $^4$He data are plotted as a function of the sampling depth in fig. 1a. Even if it is assumed that ground water recharged during the period of maximum $^3$H fallout (concentration of about 800 TU) that occurred around 1963, $^3$H decay would produce less than 1.65x10$^{-12}$ ccSTP/g $^3$He through 1992 (ccSTP/g means cubic centimeters of gas at a pressure of 1 atmosphere and 0°C per gram of water). The $^3$He$_{\text{sat}}$ fraction in the samples is about 6x10$^{-14}$ ccSTP/g. Recharge-temperature assumptions and the measured Ne concentrations produce only small variations in $^3$He$_{\text{sat}}$. Thus, an explanation of measured $^3$He concentrations above about 1.71x10$^{-12}$ ccSTP/g requires an excess He source.
In ground water contained in at least 10^7 year-old bedrock, such as that found in the Mirror Lake Basin, the in situ source of excess He is expected to be due to radioactive decay of thorium (Th) and uranium (U) in the rock matrix, producing He with a 3He/4He ratio of about 2x10^-8. The calculated amount of excess He in the water samples is given in table 1. 4He exc is dominated by the external He source; this leads to a first-order increase in the measured 4He concentration with depth as well as an increase in 4He exc (see fig. 1b). From the measured 3H concentrations as well as other geochemical data and the CFC concentrations (Busenberg and Plummer, 1996), it is known that the apparent age of most of the analyzed samples should not exceed 50 to 100 years. With an assumed concentration of 2.8 ppm U, a Th/U ratio of 3.8 and a bedrock porosity of 0.05, steady state 4He production and total release to the fluid over a period of 100 yrs years would yield 4He exc values of about 10^-10 ccSTP/g in the ground water (Torgersen and Clarke, 1985). The deep groundwater samples have 4He concentration in excess of this value, and, therefore, the obtained data can not be explained without additional in situ sources such as those found by Torgersen and Clarke (1985), Torgersen and Ivey (1985), Torgersen and others (1989), Martel and others (1989), Stute and others (1992), Hiyagon and Kennedy (1992), Marty and others (1993).

Another possible explanation for the high 4He concentrations might be mixing of very young water (containing 3H and tritiogenic 3He) and very old water with high 4He concentrations. This scenario is less probable for ground-water samples from the drift-zone but could be a potential scenario for ground water in the bedrock because of the irregular fractures in the bedrock. This might explain the close similarity of ground-water data from TR1 170-190 to those of the shallower well TR1 63, and the large difference to those of TR2 151-170 (see fig. 1), which is only about 200 m away. To produce the measured high He concentrations in ground water and rather young apparent (mixing) ages, very old ground water (high

Changes of $^3$He concentrations are plotted against depth for ground-water samples from the Mirror Lake Basin. The vertical line at $1.65 \times 10^{-12}$ ccSTP/g marks the limit of $^3$He that would be accumulated from decay of $^3$H in water with 800 TU recharged in 1963. The bars represent the best estimate for the range in $^3$He error; for low $^3$He concentrations, the error bars are smaller or equal to the symbol size.

FSE 43: well name and depth at which water was collected.

ccSTP/g: cubic centimeters of gas at 0°C and 1 atmosphere per gram of water.

Changes of $^4$He concentrations are plotted against depth for ground-water samples from the Mirror Lake Basin. The bars represent the best estimate for the range in $^4$He error; for low $^4$He concentrations, the error bars are smaller or equal to the symbol size.

FSE 43: well name and depth at which water was collected.

ccSTP/g: cubic centimeters of gas at 0°C and 1 atmosphere per gram of water.

$^4$He content) must be mixed with very young water that recharged around the time of the bomb-derived $^3$H peak (1963). Such a mixing scenario is shown in figure 2. The resulting $^3$He/$^4$He ratios of water samples can be derived for different initial $^3$H concentrations (fig. 2, numbers left of the different curves) and mixing ratios (fig. 2, numbers below the curves indicate the mixing ratio of old and young waters). Although most drift-well $^3$He/$^4$He ratios could, in principle, be explained by mixing (except the water sample from well FSE 43), most of the deeper wells would require mixing with waters with an unrealistically high initial $^3$H concentration. Therefore, mixing is an unlikely explanation for the observed He distribution in ground waters in the Mirror Lake Basin.

A plot of the $^3$He contents as a function of the $^4$He contents (see fig. 3) for the samples shows that the He supplied to the deep wells is dominated by a source that can be approximated by a He isotope ratio of $1.65 \times 10^{-16}$. This ratio is much higher than the wellknown and expected one for radiogenic He (typically around $2 \times 10^{-8}$) and, thus, an 'exotic' source of He is required to explain the measurements. Two sources could be assumed:

1. Although the local intrusive rocks are older than $10^8$ years, they might contain trapped primordial gas with a high $^3$He/$^4$He ratio normally found only in young mantle material.
2. There is a local, young source of He from the mantle that is outgassing, this He is mixing with He produced in local bedrock and is transported in ground water into the Mirror Lake Basin where it mixes with younger surface water in the bedrock.

In order to address the first possibility, rock cuttings from two drill cores (from wells at different sides of the basin) at depths $>100$ m were analyzed for the $^3$He and $^4$He content of their main components (basalt, granite, pegmatite, and schist). Samples were crushed to release the gas trapped in vesicles and fluid inclusions, and $^3$He and $^4$He contents were measured (table 2). The measured $^3$He/$^4$He ratios for bedrock are $R_{\text{rock}} = 2.2 \times 10^{-8}$ to $6 \times 10^{-7}$; these ratios are significantly
Figure 2. Plot of the He isotope ratio as a function of the He/Ne ratio for ground-water samples from the Mirror Lake Basin. Beside the measured ground-water-sample data is shown the result for a mixing of (1) 30-year-old water with only a tritiogenic and no radiogenic $^3$He component and various initial tritium-derived $^3$He values, with (2) old, radiogenic, i.e. $^4$He-enriched water with a typical $^3$He/$^4$He ratio of $2 \times 10^{-8}$. Mixing ratios are given along the x-axis corresponding to the calculated data points above (indicated by '+' for the 0 TU curve). 'plus tritio. He': The initial tritium-derived $^3$He content if no mixing with old waters has yet occurred.

Figure 3. Plot of measured $^3$He- as a function of $^4$He-concentrations for the Mirror Lake Basin ground-water samples. Air saturation for 10°C is about $5 \times 10^{-8}$ ccSTP/g for $^4$He and $6 \times 10^{-14}$ ccSTP/g for $^3$He. The plot suggests admixture of a He component with an isotope ratio of $1.65 \times 10^{-6}$. The bars represent the best estimate for the ranges in $^3$He and $^4$He errors; for low He concentrations, the error bars are smaller or equal to the symbol size.

Table 2. Helium-3/Helium-4 ratios and Helium-4 contents of bedrock samples

<table>
<thead>
<tr>
<th>Sample origin</th>
<th>Sample material</th>
<th>$^3$He/$^4$He x10^{-7}</th>
<th>$^4$He ccSTP/g/rockx10^{-7}</th>
</tr>
</thead>
<tbody>
<tr>
<td>IS1/390-395</td>
<td>basalt</td>
<td>6.00±0.30</td>
<td>1.29</td>
</tr>
<tr>
<td>FS2/330-340</td>
<td>basalt</td>
<td>5.10±0.25</td>
<td>2.06</td>
</tr>
<tr>
<td>IS1/440-445</td>
<td>granite</td>
<td>2.60±0.125</td>
<td>3.20</td>
</tr>
<tr>
<td>FS2/</td>
<td>granite</td>
<td>2.16±0.11</td>
<td>2.55</td>
</tr>
<tr>
<td>FSE13/195-200</td>
<td>pegmatite</td>
<td>4.73±0.235</td>
<td>18.53</td>
</tr>
<tr>
<td>FSE13/242-250</td>
<td>pegmatite</td>
<td>4.10±0.21</td>
<td>14.99</td>
</tr>
<tr>
<td>IS1/215-220</td>
<td>schist</td>
<td>0.22±0.15</td>
<td>27.68</td>
</tr>
</tbody>
</table>
| FS2/300-310   | schist          | 2.64±0.14              | 3.54                        | lower than those observed in waters from deep wells ($1.65 \times 10^{-6}$) and inconsistent with our hypothesis mentioned above. Therefore, local rocks are not a viable source for the excess He component observed in the water samples. The fact that the measured bedrock $^3$He/$^4$He ratios are higher than the typical radiogenic isotope ratio of about $2 \times 10^{-8}$ might at least partly be a consequence of the rock crushing procedure. Only part of in situ radiogenic He may be released during the crushing procedure, whereas primordial gas trapped in relatively larger vesicles would be more efficiently released; in fact, the basalts have the highest observed $^3$He/$^4$He ratios. It is also possible that the rock samples were incompletely cleaned of an adsorbed air component resulting in a release of He with the observed ratio of around $2 \times 10^{-7}$. This possibility will have to be verified by melting rock samples. Then radiogenic He contained in the rock matrix will be released. It should be noted that the He concentrations in the rock samples are up to $2.7 \times 10^{-6}$ ccSTP/g rock. This very high concentration,
together with the observed He isotope ratio, might be an indication of in situ radiogenic He production combined with an 'exotic' He source (preferentially high in $^3$He) and He diffusion into the rock from the fluid. This possibility also could be tested by stepwise heating and extraction of He from the rock samples.

The second possible scenario for the 'exotic' He component observed in the Mirror Lake ground-water samples could be degassing from deep, local mantle-derived rock. He-isotope studies at numerous sites suggest that the occurrence of mantle He is related to tectonically active regions (O'Nions and Oxburgh, 1983; Hooker and others, 1985; Oxburgh and others, 1986; Oxburgh and O'Nions, 1987; O'Nions and Oxburgh, 1988; Stute and others, 1992; Marty and others, 1992; Griesshaber and others, 1992). There is no recent volcanic activity in the Mirror Lake region and only limited recent seismic activity. However, observations in the Paris Basin (Marty and others, 1993) suggest that the timescale for the degassing of the mantle He component is longer than hypothesized by O'Nions and Oxburgh (1988). If this is the case, the 'exotic' He may originate from an earlier event, for example the breakup of the North Atlantic. A clearer understanding of the regional source of 'exotic' He and its transport into the ground-water from the Mirror Lake Basin will emerge when deeper ground-water samples are available for analysis and a regional vertical flux of radiogenic and exotic He can be determined.

Although the source of the excess He is unknown, $^3$H/$^3$He-based ages calculated using an excess-helium ratio of $R_{\text{exc}} = 1.65 \times 10^{-6}$ are shown in table 1. Reasonable agreement of the $^3$H/$^3$He-based ages with CFC-based ages (Busenberg and Plummer, 1996) indicates that this approach is not unreasonable. However, if $^4$He_{exc} exceeds $^4$He_{air} by more than a factor of about 4 to 5, reliable dating is not possible. Because of the heterogeneity in the bedrock and the drift zone it can not be excluded that (for example) the drift-water samples have to be treated differently. Therefore $^3$H/$^3$He-based ages calculated with $R_{\text{exc}} = R_{\text{rad}} = 2 \times 10^{-8}$ are also shown in table 1. The contribution of the two discussed He sources with $R_{\text{exc}} = 1.65 \times 10^{-6}$ and $R_{\text{exc}} = R_{\text{rad}} = 2 \times 10^{-8}$, respectively, cannot be determined and might vary. It should be noted that the resulting ages are very sensitive to changes in $R_{\text{exc}}$ if that ratio exceeds about $1 \times 10^{-6}$.

Because the calculated ground-water ages and the He content of most of the samples increase with depth, the He concentration itself may carry age information, as shown in figure 4 where the calculated $^3$H/$^3$He-based ages are plotted against measured $^4$He concentrations. The shape of that curve is nearly exponential and may reflect a flux of He through the local bedrock. This hypothesis would be supported by more data points from deeper wells; by use of CFC data (Busenberg and Plummer, 1996); and additional age-dating tools, such as $^{85}$Kr-based age dating (Smethie and others, 1992) or flow-path analysis using other dissolved chemical compounds and the results of the hydraulic tests.

REFERENCES


Figure 4. Plot of excess helium (He_{exc}) as a function of $^3$H/$^3$He-based ground-water ages for the Mirror Lake Basin samples for the two assumptions of the $^3$He/$^3$He ratio of the excess helium source, $R_{\text{exc}}$. It could be that the best assumption for $R_{\text{exc}}$ varies from sample to sample and the plotted results of the two assumptions reflect only an age range. Note, that the $^4$He concentrations (see fig.1B), and, at least tententially, the $^3$H/$^3$He-based ages (and CFC-based ages, not shown here) increase with depth in the aquifer.


Observational, Experimental and Inferred Evidence for Solute Diffusion in Fractured Granite Aquifers: Examples from the Mirror Lake Watershed, Grafton County, New Hampshire

By Warren W. Wood¹, Allen M. Shapiro¹, Paul A. Hsieh², and Terry B. Councell¹

Abstract

The role of solute diffusion between ground water and granite in the Mirror Lake drainage area was evaluated by direct observation, experiment, and inference. The outcrops display ubiquitous Liesegang bands associated with fractures that clearly indicate the activity of diffusion in this system in the past. Laboratory experiments determined that the effective diffusion coefficient for ¹³⁷Cs was approximately $6 \times 10^{-13}$ m²/s in granite from Mirror Lake. The Cs penetrated to a depth of approximately 7 mm in 101 days, demonstrating the potential for rapid diffusion in this system. Porosities of 32 granite samples averaged of 1.46 percent with a range of 1.07 to 2.32 percent. Measurements of carbon-isotope of ground water in the fractures suggest that calcite, identified in the granite, is dissolving and the bicarbonate generated is diffusing to the fractures; that is, a significant amount of the dissolved solids in the water in the fractures are derived from diffusion of weathering products from the rock matrix. These observations taken together are consistent with the interpretation that diffusion is a major process controlling solutes in this fractured granite aquifer.

INTRODUCTION

Diffusion can be an important mechanism controlling solute transport in ground water in fractured crystalline rocks even if ground water residence times in the fractures are relatively short. In order to evaluate effects of diffusion in a fractured rock system, we studied a natural, hydrologically and chemically unstressed igneous and metamorphic terrane in the Mirror Lake watershed near West Thornton, Grafton County, New Hampshire (42° 56' N, 71° 43' W). In this paper we first visually and petrographically describe the granite for evidence of diffusion, conducted laboratory experiments to determine diffusion coefficients and evaluated solute concentration in the fractures for evidence of diffusion. The geology, and general hydrology of this site is described by Winter (1984). Low permeability glacial tills provides storage whereas the fractures in the underlying crystalline rock are the main conducts for regional ground-water flow. The residence time for flow in fractures in the upper 150 m of the crystalline rock is relatively short. Ninety six of the 100 ground-water samples collected from the fractured bedrock indicate residence times of less than 50 years on the basis of concentrations of chlorofluorocarbons, manufactured since the late 1930’s, and tritium from atmospheric testing of thermonuclear devices in the 1950’s and early 1960’s. These samples were collected from hydraulically isolated intervals in bedrock wells at depths ranging of 50 to 150 m below the rock surface.

OBSERVATIONAL EVIDENCE FOR DIFFUSION

Observational evidence for diffusion in this system was obtained at the I-93 (Interstate Highway 93) road cut on the eastern side of the Hubbard Book drainage area. At this exposure, numerous conspicuous ferri hydroxide “Liesegang bands” are formed parallel to many of the fractures and are known to form as a result of the diffusion processes (Berner, 1971). In this system, we hypothesize that the bands of ferric hydroxide are formed by the reaction of ferrous iron, produced by the weathering of the ubiquitous am-phiboles and biotites, with oxygen as it diffuses into the rock from the fracture. Analytical solution of the diffusion equation, with appropriate boundary and initial conditions, demonstrates that the ferric hydroxide bands can form in response to fluctuating oxygen concentration in the fracture. Furthermore on the basis of measured diffusion coefficients and observed concentrations of iron and dissolved oxygen the bands will form in times of tens to hundred of years. Thus, diffusion has operated

EXPERIMENTAL EVIDENCE FOR DIFFUSION

Experimental evidence in support of diffusion was collected in a series of laboratory experiments on representative samples of granites, schists, and basalts from the Mirror Lake area. The diffusion coefficient was measured on 3-cm cubes cut from the unweathered part of large samples collected from fresh outcrops at the I-93 road cut. One face of the cube was polished with fine 1200 mesh carborundum grit, washed in distilled water, dried in a vacuum oven at 50 °C for 3 days and weighed. The cubes were then placed in a CO₂ pressurized chamber for 1 week to replace the slightly soluble air with highly soluble CO₂. Samples were then placed in a distilled-water bath at room temperature for 6 months and then, removed; their surfaces were then blotted dry and the sample weighed. Background radioactivity was measured using a sodium iodide crystal and multi-channel analyzer in the energy range of 137Cs. The five unpolished surfaces on each cube were covered with paraffin wax and placed in a solution containing 137Cs with an activity of 26 disintegrations per milliliter per second.

After 101 days, three replicates of each rock type were withdrawn, the wax was removed, and the five waxed sides of the cube were lightly ground using a diamond surfaced lapidary wheel to remove any 137Cs that might have penetrated between the wax and the rock. The rock was then dried in a vacuum oven at 50 °C for 3 days, stopping the diffusion of 137Cs until the sample could be analyzed. Radioactivity of the samples was then measured and distance determined from the exposed polished face to the back face by means of a micrometer. The polished face of the sample was then lightly ground using a coarse, 100-mesh lapidary polishing wheel, measured with the micrometer to determine thickness of material removed, weighted and radioactivity measured. This procedure was repeated numerous times until there was no change in the activity of 137Cs with successive grindings.

Initially there was concern that polishing the face would create microfractures that would artificially increase the diffusion rate. To evaluate this, we performed a replicate experiment similar to that described above only with pairs of cubes, one having a natural fracture face and the other a polished face. After 3 days of soaking, the cube with the polished face had greater depth penetration of 137Cs, however, after 10 days the penetration was the same in both cubes. Thus, we conclude that for our relatively long soaking period that we did not significantly bias the sample by polishing the exposed face. However, it can be seen in figure 1 that the activity ratio for penetration depths less than 3 mm are slightly higher than the theoretical curve suggesting some effect of polishing, but the effect is small and does not alter significantly the overall fit of the observed data to the theoretical curve.

To evaluate the effective diffusion coefficient from these experiments, consider the equation of mass conservation for a sorbing solute,

$$\frac{\partial (\theta C + \rho s)}{\partial t} = D \frac{\partial^2 C}{\partial x^2}.$$  

where C is the aqueous phase concentration of the solute (M/L³), θ is the porosity (L³/L³), ρ is the bulk density of the solid (M/L³), s is the mass of the sorbed solute per unit mass of the solid phase (M/M), D is the effective diffusion coefficient (L²/T), t is time (T), and x is the spatial coordinate (L). M, L and T denote units of mass, length and time, respectively. If the concentration of the sorbed solute is proportional to the aqueous phase concentration, s = kC, where k is the sorption coefficient (L³/M), the equation of mass conservation can be rewritten as

$$\frac{\partial C}{\partial t} = \frac{D \rho^2 \theta}{R} \frac{\partial^2 C}{\partial x^2}.$$  

where R is the retardation coefficient (1 + ρk/θ).

Because diffusion does not penetrate far we may assume a semi-infinite domain. With an initial condition of C=C₀ and boundary conditions C(x=0,t)=C₀ and ∂C/∂x (x→∞,t) = 0, the solution to the previous equation is

![Figure 1. Graph showing the activity of cesium-137 observed in the rock (A) to activity in the solution (A₀) as a function of the depth of penetration of the cesium-137 for granite from Mirror Lake after 101 days of exposure. Also illustrated is a modeled range of effective diffusion coefficients, in m²/s, that bracket the observed data.](image-url)
where \( \text{erfc} \) is the complementary error function.

Because of the experimental procedure of drying the samples prior to measurements, the activity of \(^{137}\text{Cs}\) is measured on the solid only which is denoted as \( m = \theta C(x,t) + \rho s = \theta RC(x,t) \). Using equation (3), the combined concentration of the fluid and solid phase concentration is

\[
m(x,t) = \theta RC_0 \text{erfc} \left[ \frac{x}{2 \sqrt{(Dt/R_0)}} \right].
\]

Assuming the \(^{137}\text{Cs}\) activity is directly proportional to the \(^{137}\text{Cs}\) concentration, then the ratio of activities, \( A/A_0 \), is equal to the ratio of concentrations, \( m(x,t)/\theta RC_0 \). Because the sorption coefficient, \( k \), is large, the \(^{137}\text{Cs}\) sorbed on the solid phase is large in comparison to that in solution. Thus, \( A_0 \) is defined as the difference between the initial activity of the entire rock sample and the activity measured after the first grinding of the rock face. That is, it is assumed that the first section of the rock face is in equilibrium between the solute and the solid. The activity of the remaining sections of the rock are defined by the difference between the activities of the successive grindings of the rock sample. These values are associated with positions that are 1/2 the measured distance between successive sections of the removed rock.

Results of this diffusion experiment for a granite sample are shown in figure 1, where the relative activity, \( A/A_0 \), of \(^{137}\text{Cs}\) is plotted as a function of the depth of penetration into the sample. The activity is expressed in disintegration's per second per gram of removed solid. The coefficient which best determined the spatial distribution shown in figure 1 is \( 6 \times 10^{-13} \text{ m}^2/\text{s} \). It can be seen that this value is well constrained within a narrow range of potential values. This value incorporates the effects of the porosity and tortuosity of the void space in the sample, as well as the retardation of \(^{137}\text{Cs}\). This value is similar to the value of \( 1 \times 10^{-13} \text{ m}^2/\text{s} \) which was determined by Skagius and Neretnieks (1988) for \(^{137}\text{Cs}\) in a biotite gneiss from Sweden.

The effective diffusion coefficient, \( D/R_0 \), for \(^{137}\text{Cs}\) in basalt was determined by the same method and was found to average \( 2 \times 10^{-14} \text{ m}^2/\text{s} \). The difference between the effective diffusion coefficient of the granite and basalt samples is related to the difference in porosity, tortuosity and retardation coefficient. The porosity of the granite is 4 to 5 times larger than that of the basalt and is the major factor in the differences.

Porosities were determined from the difference between wet and dry weights of the sample cubes described above and assuming a bulk density for the samples [granite 2,640 kg/m\(^3\); basalt 2,850 kg/m\(^3\)]. Average porosity for 32 samples of granite was 1.46 percent with a range from 1.07 to 2.33 percent. The average porosity for 15 samples of basalt was 0.36 percent and ranged from 0.58 to 0.24 percent. Porosity of 23 samples of schist averaged 1.87 percent and ranged from 1.07 to 3.36 percent.

**INFERRED EVIDENCE OF DIFFUSION**

Evidence of inferred diffusion in this system is shown by concentrations of bicarbonate, stable carbon isotopes, and presence of calcite in the rock. Alkalinity in this geochemical system is almost exclusively a function of the bicarbonate ion (\( \text{HCO}_3^- \)) that formed by weathering reactions of carbonate and silicate minerals with soil carbon dioxide. For example, the weathering of calcite (\( \text{CaCO}_3 \)) to \( \text{Ca}^{++} \) (calcium) and bicarbonate (\( \text{HCO}_3^- \)) carbonic acid (\( \text{H}_2\text{CO}_3 \)) is given by

\[
\begin{align*}
\text{CO}_2 + \text{H}_2\text{O} \quad &\quad \downarrow \\
\text{CaCO}_3 + \text{H}_2\text{CO}_3 \quad &\quad = 2\text{HCO}_3^- + \text{Ca}^{++}
\end{align*}
\]

We observed concentrations and isotopic signatures of bicarbonate that could only be the result of dissolution of carbonate minerals. Yet there is no calcite or other carbonate mineral presently in the fractures. If there were some at one time, they have been dissolved. Thus, we hypothesize that bicarbonate is generated by weathering of calcite in the rock and is diffusing from the rock matrix to the fracture.

Calcite was identified in small grains in the rock matrix by petrographic evaluation, scanning electron microscope (SEM) and energy dispersive X-ray analysis (EDAX) of cores and outcrop samples. Total carbon analysis of a granite sample from the I-93 road cut yielded 0.12 percent carbon. It is assumed that this carbon is from the calcite identified by SEM and EDAX.

Evidence for dissolution of calcite is shown by the increase in isotopically heavy carbon with increasing alkalinity (fig. 2). Water in this system is generally thermodynamically under-saturated with respect to calcite below an alkalinity of approximately 125 mg/L. Thus, if calcite were present it would dissolve. The average stable carbon isotopes in five soil \( \text{CO}_2 \) gas samples collected in the watershed had a \( \delta^{13}\text{C} \) of -22 %/oo relative to that in belemnitella americana from the Cretaceous Pedee Formation (PDB). Because there is a fractionation factor of approximately 8 %/oo at the ambient temperature of this system, bicarbonate ions in the water will have a \( \delta^{13}\text{C} \) value of approximately -14 %/oo in equilibrium with a soil gas of -22 %/oo. Thus, weathering of silicate mineral by carbonic acid would yield a \( \delta^{13}\text{C} \) in the water of -14 %/oo because there is no other
source of carbon. However, if weathering of a carbonate mineral by carbonic acid occurs, there are two sources of carbon: one from the carbonic acid and one from the carbonate mineral. Because carbonate minerals typically have a $\delta^{13}C$ near zero, the $^{13}C$ dissolved in the water as the bicarbonate ion reflects both sources of carbon as indicated in the above equation. Thus, at equilibrium, the $\delta^{13}C$ carbon isotopes determined in the water will have a value near -7 o/oo (one carbon atom from the mineral $\delta^{13}C = 0$ and one from the carbonic acid $\delta^{13}C = 14$).

Also consistent with diffusion of bicarbonate is the strong correlation between residence time determined from chlorofluorocarbon dating (Busenberg and Plummer, 1992) and concentration of alkalinity (fig. 3), that is, the younger water is thermodynamically undersaturated with respect to calcite, which would rapidly dissolve if exposed to this water. The fact that it has taken tens of years to approach equilibrium is consistent with transport by diffusion.

We propose the following generalized conceptual model for diffusion in this crystalline fractured system. Overburden water, low in total dissolved solids, alkalinity, pH and thermodynamically undersaturated with respect to calcite and saturated with dissolved oxygen enters the fractures. Oxygen and carbonic acid diffuses from the fracture into the rock matrix where biotites, pyroxenes, calcite, and feldspars are weathered consuming oxygen and carbonic acid and forming ferrous iron and bicarbonate ions among other products. Interaction of the iron diffusing from the rock matrix to the fracture with the oxygen diffusing from the fracture to the rock matrix, causes iron to precipitate as ferric hydroxide and form the observed Liesegang bands. Rate of weathering, diffusion rates and concentration of dissolved oxygen in the fracture control distance of the bands from the fracture. Bicarbonate generated by dissolution of calcite diffuses to the fracture giving the observed $\delta^{13}C$ signature.

**SUMMARY**

In summary, three independent lines of evidence suggest significant solute diffusion in this system. Paleodiffusion in the form of ferric hydroxide Liesegang bands is consistent with assumption of diffusion into and out of the rock matrix. Laboratory determined diffusion coefficients and porosity values suggest that the observed concentration gradients will provide significant flux of solutes into and out of the rock in a relatively short time. And finally stable isotopes of carbon provide evidence of calcite dissolution while SF$_{6}$ and petrographic analyses identified calcite in the granite.

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A Conceptual Model for Estimating Regional Ground-Water Velocity in Bedrock of the Mirror Lake Area, Grafton County, New Hampshire

By Allen M. Shapiro¹, Warren W. Wood¹, Eurybiades Busenberg¹, Stefan Drenkard², L. Niel Plummer¹, Thomas Torgersen³, and Peter Schlosser²

Abstract

Estimation of regional ground-water velocities requires a knowledge of the residence time of the ground water and the distance it has traveled. Ground-water residence times are estimated in the Mirror Lake area on the basis of concentrations of chlorofluorocarbons and the parent-daughter isotopes tritium and helium. The distance the ground water has traveled, however, cannot be identified in the Mirror Lake area because there is no single area of recharge to the bedrock and the heterogeneity of hydraulic properties of the bedrock indicate that a regional flow line cannot be conceptualized from successive down-gradient sampling locations. Measurements of alkalinity in water samples collected from fractures in the bedrock are positively correlated with ground-water age. The alkalinity is controlled by the concentration of bicarbonate ions, and carbon isotopes indicate that the bicarbonate concentration is the result of dissolution of calcite in the rock matrix. The diffusion of bicarbonate ions from the rock matrix to fractures is hypothesized as a second indicator of the residence time of ground water in the bedrock. A simple model of ground-water flow and the transport of bicarbonate ions in the bedrock is proposed to investigate the relation among ground-water velocity, residence time and alkalinity. The model consists of a single fracture in contact with a rock matrix from which the average ground-water velocity in the bedrock can be estimated. From this simple conceptual model, the length of paths of fluid movement in the bedrock and the average bedrock velocity can be estimated. This conceptual model, however, must be reconciled with other geochemical data that indicates that ground waters of various ages are mixing either naturally or as a result of ground-water sampling.

INTRODUCTION

In shallow ground-water systems, concentrations of chlorofluorocarbons (CFC's), and the parent-daughter isotopes tritium and helium can be used to estimate ground-water ages (Busenberg and Plummer, 1992; Schlosser and others, 1988; Solomon and others, 1992). Ground-water ages estimated by these environmental tracers represent the residence time of the water since it was last in contact with the atmosphere. However, the distance the ground water has traveled within that time also must be identified to estimate the ground-water velocity. In the absence of a single, well-defined recharge location, additional hydrologic, geologic, and geochemical information must be used to infer the length of the ground-water-flow paths. In this article a simple model is conceptualized to estimate rates of ground-water flow using geologic and geochemical information, and the results of CFC and tritium-helium age dating of water samples collected from the glacial drift and the upper 200 m of the bedrock in the Mirror Lake area in Grafton County, New Hampshire (fig. 1).

SITE DESCRIPTION

The Mirror Lake watershed is located at the mouth of the Hubbard Brook valley in the southern part of the White Mountains of central New Hampshire (fig. 1). Its area is approximately 85 ha; Mirror Lake covers an area of approximately 15 ha. The elevation of Mirror Lake is approximately 213 m above sea level; the highest elevations in the watershed

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The bedrock in the Mirror Lake area is a sillimanite-grade schist that has been extensively intruded by granite and pegmatite and lesser amounts of basalt. Successive orogenies have caused folding and faulting resulting in extensive fracturing of the bedrock. Roadcuts exposed along Interstate Highway 93, east of Mirror Lake, show poorly connected fractures and irregular configurations and dimensions of schist, granite, pegmatite and basalt (Barton, 1996). In most areas of the Mirror Lake watershed, the bedrock is overlain by unconsolidated glacial deposits (drift) up to 50 m thick. In general, ground water flows from higher elevations north and west of Mirror Lake to lower elevations, where ground-water discharges, such as Mirror Lake, perennial streams in the vicinity of Mirror Lake, and the Pemigewasset River east of Mirror Lake. A more detailed discussion of the hydrogeology of the Mirror Lake area is provided by Winter (1984; 1985).

Wells in the bedrock and piezometers in the glacial drift have been installed in the Mirror Lake area to investigate regional ground-water flow (fig. 1). Each bedrock well is drilled and cased through the glacial drift and the upper 3 m of the bedrock, and a 0.15-m-diameter open hole extends into the bedrock to the desired depth. Depths of bedrock wells in the Mirror Lake area range from 60 to 230 m. At most bedrock-well sites, one or more 0.05-m-diameter drift piezometers, each with a 0.6-m-long screened interval, were installed at various depths in the saturated part of the drift above the bedrock surface. A petal-cement basket is installed above the screened interval and the annular space between the piezometer casing and the drill hole is grouted (Winter, 1984). Water-table wells in the drift (the screens of which intersect the water table) also were installed in the vicinity of most bedrock wells. Water levels have been recorded in water-table wells, drift piezometers, and in hydraulically isolated intervals of bedrock wells (Hsieh and others, 1996).

GROUND-WATER AGES

Water samples for geochemical and isotopic analysis (including concentrations of CFC's, tritium, and helium) were collected from selected fractured intervals in 14 bedrock wells and from a selected number of drift piezometers in the Mirror Lake area. In bedrock wells, water samples were collected by means of a piston pump located between packers that isolated a discrete, permeable interval of the well. In newly drilled bedrock wells, water samples were collected from isolated permeable intervals immediately after drilling and after the well was purged. In existing bedrock wells, the permeable intervals where samples were collected were isolated for up to a year by use of inflatable packers to prevent the short-circuiting of water from fractures in which hydraulic heads differed. Water samples also were collected from drift piezometers by means of a submersible or peristaltic pump. Of the more than 80 discrete bedrock and overburden intervals that were sampled, only 10 of the intervals yielded ground water containing no tritium which indicated that the ground-water ages exceeded 45 years.

A preliminary interpretation of ground-water ages was made on the basis of concentrations of dichlorodifluoromethane (CFC-12), trichlorofluoromethane (CFC-11), and trichlorotrifluoroethane (CFC-113) (Busenberg and Plummer, 1996). Estimates of ground-water ages from concentrations of the parent-daughter isotopes tritium and helium were made for samples from drift piezometers and the shallowest intervals of the bedrock wells (Drenkard and others, 1996). Estimates of ground-water ages from concentrations of the parent-daughter isotopes tritium and helium were made for samples from drift piezometers and the shallowest intervals of the bedrock wells (Drenkard and others, 1996). The ground-water ages estimated from the tritium-helium and CFC analyses compare well with one another (Drenkard and others, 1996). However, the estimated ages do not correspond well with the presumed date of the maximum known atmospheric-tritium concentration. Both the tritium-helium and CFC interpreted ages appear to be approximately 6 years younger than ground-water ages that would be estimated by using the maximum known tritium concentration as the date of the maximum atmospheric tri-
tium concentration (Busenberg and Plummer, 1996). This difference is still being investigated and may be the result of ground-water flow through the unsaturated zone, where the air phase can allow further equilibration with the atmosphere, or the difference may be a result of the mixing of waters of various ages (either naturally or during the collection of water samples).

The ages of ground-water samples collected in July and August of 1992 from bedrock wells R-1, TR-2 and T-1 are shown in figure 2. Younger ground-water ages were found at several deeper sampling locations. In addition, younger ground-water ages were found at locations closer to Mirror Lake which is an area of ground-water discharge. The variation in hydraulic head reflects changes in topography, implying that the direction of ground-water flow in the bedrock is toward Mirror Lake. In addition, the hydraulic head data suggest that the cross-section through the three bedrock wells in figure 2 could be hypothesized as a regional flow line. However, the ground-water ages indicate that fluid movement in the bedrock is a complex, three-dimensional process where a line of wells cannot be conceptualized as being along a regional flow line. The complexity of the flow regime is also supported by the variability of hydraulic properties of the bedrock (Hsieh and Shapiro, 1996), and the poor fracture connectivity that has been demonstrated in mapped fractures on bedrock outcrops and road cuts in the Mirror Lake area (Barton, 1996).

**GROUND-WATER CHEMISTRY AND RESIDENCE TIME**

Because recharge is areally distributed, the distance the ground water has moved to reach each sampling location is not identifiable. In addition, the distance between successive down-gradient sampling locations and the differences in ground-water ages at sampling points can not be used to estimate the ground-water velocity, because successive down-gradient sampling locations can not be interpreted as a regional flow line because of the heterogeneity of the hydraulic properties of the bedrock. In order to address the question of the length of flow paths associated with the sampling locations where ground-water ages have been estimated in the Mirror Lake area, we consider other geochemical evidence to indicate ground-water residence times.

Evidence indicates that diffusion from the rock matrix to fractures plays an important role in the chemistry of the ground water in the bedrock of the Mirror Lake area (Wood and others, 1996). The total dissolved solids concentration in water samples collected from overburden piezometers averages approximately 50 mg/L, whereas the total dissolved solids concentration in water collected from fractures in the bedrock is significantly higher, averaging approximately 250 mg/L. Residence times of less than 45 years in the shallow bedrock are not sufficient for the dissolution of minerals characteristic of granite or schist along fracture faces to cause this increase in dissolved solids. Instead, it is hypothesized that water in the void space of the unfractured granite and schist is in chemical equilibrium with the associated minerals in the granite and schist. These equilibrium concentrations are significantly larger than the concentrations of dissolved solids in the water recharged through the overburden and into the fractures in the bedrock. Thus, the concentration gradient between fluid in the rock matrix and fluid in the fractures results in the mass flux of dissolved solids into the fractures.

The alkalinity of water samples collected from fractures in the bedrock offers additional evidence as to the role of diffusion in the chemistry of ground water (Wood and others, 1996). The alkalinity of water samples extracted from fractures in the bedrock is almost exclusively a function of the bicarbonate ion (HCO$_3^-$). As discussed in Wood and others (1996), isotopic signatures of carbon indicate that the bicarbonate ion is derived from the dissolution of carbonate minerals, yet there is no known evidence of calcite in fractures. However, calcite was identified in granite samples from cores and outcrops (Wood and others, 1996). The total carbon in granite samples from outcrops was 0.12 percent of the sample weight. If all carbon is assumed to bound in calcite, then approximately 1 per-
cent of the rock matrix is calcite by weight. Wood and others (1996) also measured other properties that affect diffusion from the rock matrix, including porosity and the effective diffusion coefficient.

A comparison of alkalinity and ground water ages shows a positive correlation (fig. 3). Figure 3 shows that water samples from the drift have low alkalinity and young ground water ages. Water samples collected from fractures in bedrock indicate that alkalinity increases with ground-water age, but the alkalinity is bounded by the saturated concentration of bicarbonate ions in the ground water. Therefore, we hypothesize that bicarbonate ions are diffusing from water in the rock matrix and into fractures, and the bicarbonate concentration is a function of the residence time associated with ground-water flow in the fractures. The estimate of the equilibrium bicarbonate concentration shown in figure 3 was calculated by means of the geochemical-analysis program PHREEQE (Parkhurst and others, 1980), whereby a representative solution of overburden water was reacted with calcite and a partial pressure of carbon dioxide calculated from the chemistry of the overburden water.

**ESTIMATING THE LENGTH OF GROUNDWATER FLOW PATHS IN BEDROCK**

In order to investigate the relation among alkalinity and ground-water velocity and residence time, we consider a simplistic and preliminary conceptual model of ground-water flow and the transport of bicarbonate ions through the bedrock (fig. 4a). The model consists of a single fracture. Ground water is advected through the fracture with a specified velocity. The bicarbonate concentration at the inlet to the fracture is representative of the overburden water (18 mg/L). We assume that there is no dispersion in the fracture; however, as the ground-water is advected along the fracture, bicarbonate ions diffuse from the rock matrix to the fracture because of the concentration gradient. The gradient depends on the bicarbonate concentration in the fracture and the position of a calcite-dissolution front in the rock matrix. Assuming that the dissolution of calcite in the rock matrix is not kinetically controlled, calcite dissolution will occur as a sharp front (Rubin, 1983; Willis and Rubin, 1987). Between the fracture and the calcite dissolution front, the bicarbonate concentration is controlled by the diffusion equation. At positions farther into the rock matrix, the bicarbonate concentration in equilibrium with solid-phase calcite is assumed to prevail (122 mg/L).

At the inlet to the fracture, additional calcite dissolution occurs because of the difference between the bicarbonate concentration of the overburden water and that of the water in the rock matrix. Thus, the calcite-dissolution front will be farther from the fracture at the inlet than at locations farther down-gradient. The distribution of the bicarbonate concentration along the length of the fracture is a function of the ground-water velocity through the fracture. For an infinite velocity, the bicarbonate concentration along the fracture will be constant and equal to the concentration of the overburden water, because the advective flux through the fracture will be infinite.

**Figure 3.** Ground-water ages estimated from CFC-12 concentrations and alkalinity of water samples collected from bedrock wells and drift piezometers in the Mirror Lake area.

**Figure 4.** (a) Conceptual model of calcite dissolution and bicarbonate diffusion from a rock to a single fracture. (b) Bicarbonate concentration after 1000 years as a function of distance along a fracture for three ground-water velocities.
fracture will be large relative to the diffusive flux from the rock matrix. For a zero flow velocity, the bicarbonate concentration in the fracture will achieve the saturated bicarbonate concentration associated with the rock matrix. Velocities between these two extremes will yield distributions of bicarbonate concentration as a function of the distance along the fracture.

The distribution of the bicarbonate concentration along the fracture also depends on the time since the initial conditions. For example, if the initial calcite-dissolution front is assumed to coincide with the fracture face, and the initial bicarbonate concentration in the fracture is assumed to be the saturated bicarbonate concentration, the distribution of the bicarbonate concentration in the fracture will depend on the time after these initial conditions. For example, in figure 4b, assuming the initial conditions discussed above, the bicarbonate concentration along a fracture is shown after 1,000 years for three values of the groundwater velocity in the fracture. These calculations were made using a sharp-interface model for calcite dissolution in the rock matrix as discussed in Willis and Rubin (1987). The bicarbonate concentration in the fracture was calculated by a one-dimensional finite-difference approximation for time-dependent advective transport subject to diffusion from the rock matrix. Longer elapsed times do not appreciably affect the distribution of the bicarbonate concentration along the fracture for the velocities of 10-4 and 10-2 m/d. For a velocity of 10-3 m/d and longer elapsed times, the position along the fracture where calcite dissolution occurs is shifted farther from the fracture inlet than that shown in figure 4b. This results in a different distribution of bicarbonate concentrations along the fracture, which, in turn affects the calculations of the length of the flow path. The sensitivity of the elapsed time to the calculation of the distance ground water has traveled along the fracture is being investigated to place bounds on the calculations.

From figure 4b, estimates of the flow-path length associated with a specific sampling location can be made on the basis of the ground-water age and the bicarbonate concentration measured at that sampling location. For example, a bicarbonate concentration of 40 mg/L could be associated with each of the profiles of bicarbonate concentration that were generated from the three velocities in figure 4b. For each velocity, there is a unique distance from the fracture inlet where that bicarbonate concentration will be present. Because we assume that there is no dispersion in the fracture, the distance a parcel of ground-water moves in the fracture also can be defined as the product of the ground-water velocity and the residence time measured by ground-water age dating. Because the conceptual model only considers transport in the bedrock, the measured residence time must be adjusted to account for transport through the unconsolidated glacial deposits; in the Mirror Lake area residence times in the drift range from 5 to 18 years (Busenberg and Plummer, 1996). The product of the (assumed) ground-water velocity and the (adjusted) residence time can be compared with the distance along the fracture shown in figure 4b for the (assumed) ground-water velocity and the measured bicarbonate concentration. A ground-water velocity is chosen such that the two calculations for the length of the flow path in the bedrock are equal. Preliminary results from selected sampling locations show that the length of flow paths in the bedrock range from 5 to 500 m with velocities of 10^{-3} and 10^{-2} m/d. The calculation for all of the sampling locations and the sensitivity of these calculations to the travel time through the overburden and the assumed elapsed time since the initial conditions are currently being investigated.

Although this preliminary conceptual model allows us to investigate the significance of the ground-water velocity and ages in relation to bicarbonate concentrations, it is highly idealized and subject to uncertainties. The conceptual model assumes a constant velocity through an individual fracture, whereas, in reality transport in the bedrock occurs through a network of interconnected fractures of variable hydraulic properties. Also, the modeled bicarbonate distribution along the fracture is the result of an elapsed time since assumed initial conditions. The bicarbonate concentration differs with elapsed time and tectonic conditions where new fractures open and the flow regime changes in the bedrock over time. Furthermore, the correlation of the measured bicarbonate concentration and ground-water ages is not perfect and may not be assessable by the simple conceptual model considered in this article.

In addition, the conceptual model of flow and chemical transport in the bedrock only considers advective transport in the fracture. However, other geochemical data indicate the possibility of mixing of ground waters of various ages. For example, the maximum measured tritium concentration in ground-water samples is 35 TU. However, the maximum tritium concentration in 1992 should be approximately 300 TU on the basis of the peak tritium concentration in precipitation in the 1960's. Either the resolution of the sampling locations has not resolved the peak tritium concentration, or
the mixing of water of various ages reduces tritium concentrations. Also, excess helium concentrations reported by Drenkard and others (1996) are indicative of the mixing of older ground waters. The conceptual model discussed in this article needs to be reconciled with this geochemical evidence.

SUMMARY

A simple conceptual model of ground-water flow and the transport of bicarbonate ions in ground-water in the bedrock of the Mirror Lake area is proposed to estimate regional ground-water velocities. Concentrations of CFC's and the tritium-helium ratio are used to estimate the residence time of ground-water samples collected in the glacial drift and the upper 200 m of the bedrock. However, the distance the ground-water has traveled also is needed to identify the ground-water velocity. The complex flow regime in the shallow bedrock prohibits an independent estimate of the length of a flow path in the bedrock. Alkalinity of ground-water samples (caused primarily by the diffusion of bicarbonate ions from the rock matrix) shows a positive correlation with ground-water ages. Thus, the bicarbonate concentration is used as second indicator of ground-water residence time in the bedrock. A simple conceptual model consisting of a single fracture in the rock matrix is used to investigate the relations among bicarbonate concentration and ground-water velocity and residence time in the bedrock. From this conceptual model, the average ground-water velocity in the bedrock can be identified from measured bicarbonate concentrations and estimated ground-water ages. This model is currently being applied to the data collected in the Mirror Lake area. However, the conceptual model must be reconciled with other geochemical information, which indicates that the mixing of ground waters of various ages is occurring either naturally or as a result of ground-water sampling.

REFERENCES


Overview of Research at the Cape Cod Site: Field and Laboratory Studies of Physical, Chemical, and Microbiological Processes Affecting Transport in a Sewage-Contaminated Aquifer

By Denis R. LeBlanc

Abstract

The Cape Cod Toxic-Substances Hydrology research site in Falmouth, Mass., is the focus for multidisciplinary field studies of the physical, chemical, and microbiological processes affecting transport in a sewage-contaminated sand and gravel aquifer. Past and current research at the site is summarized in a synopsis of 62 papers. Past research has examined the distribution and fate of contaminants in a sewage plume that is more than 4.5 kilometers long and originates from the Otis Air Base wastewater-treatment facility. Current research includes efforts to characterize specific physical, chemical, and microbiological processes affecting transport and fate of solutes, bacteria, and protozoa at the site. These processes are characterized by means of laboratory experiments, such as batch and column tests; field experiments, such as natural-gradient tracer tests; and investigations of the sewage plume. The results of the research show the importance of physical and chemical heterogeneity, limited dispersion, and chemical processes at the sediment-water interfaces in determining the fate of contaminants in this aquifer.

INTRODUCTION

The U.S. Geological Survey (USGS) Cape Cod Toxic-Substances Hydrology research site is located in the northern part of Falmouth, Mass. (fig. 1). This site is the focus for multidisciplinary field studies of the physical, chemical, and microbiological processes affecting the movement of contaminants in a sewage plume originating from Otis Air Base. It was selected for study as part of a nationwide program of the USGS to describe the transport and fate of contaminants in the subsurface. The purpose of this paper is to review past research efforts at the Cape Cod site and to introduce the research topics discussed in other papers in this proceedings. Earlier summaries of research at the Cape Cod site can be found in reports by LeBlanc (1984b), Franks (1987), Ragone (1988), Mallard and Ragone (1989), and Mallard and Aronson (1991).

SITE DESCRIPTION

The study area is on a broad sand and gravel glacial-outwash plain that was formed during the last Pleistocene glacial retreat. The outwash plain slopes southward to Nantucket Sound and is pitted with many kettle holes, some of which contain ponds. The area contains several valleys that transect the plain from north to south. Most of these valleys do not contain streams but have wetlands at their southern ends.

The top 30 to 50 m (meters) of outwash are composed of stratified, medium to coarse sand with some gravel. The sand and gravel overlies fine sand and silt that locally contains lenses of clay, silt, sand, and gravel. These unconsolidated sediments overlie a crystalline (granodiorite) bedrock surface, which generally slopes to the southeast through the study area.
Figure 1. Location of study area, showing sewage plume, water-table contours, and tracer-test site.
On the basis of measured values for similar sediments on Cape Cod, LeBlanc (1984c) estimated that the horizontal hydraulic conductivity of the sand and gravel in the study area ranges from 60 to 90 m/d (meters per day). Results of an aquifer test conducted in the study area in 1984 indicate that the horizontal hydraulic conductivity of the sand and gravel may locally be as high as 120 m/d (Garabedian and others, 1988). The horizontal hydraulic conductivity of the underlying fine sand and silt is estimated to be about one-tenth that of the sand and gravel (LeBlanc, 1984a). The crystalline bedrock is assumed to have a very low hydraulic conductivity; therefore, the bedrock is considered to be the bottom of the regional ground-water flow system.

Ground water in the unconsolidated sediments is under unconfined (water table) conditions. The water table slopes toward the south at about 1.5 m/km (meters per kilometer) (fig. 1). Seasonal variations in recharge from precipitation produce an annual water-table fluctuation of 0.3 to 0.9 m; the highest levels are in the spring and the lowest are in the fall.

Ground-water recharge to the study area occurs primarily from precipitation and underflow from upgradient areas. Little surface-water runoff occurs because the sandy soils are very permeable. Estimated recharge to the aquifer is 0.5 meters per year, or about 45 percent of the total precipitation (LeBlanc, 1984a). Estimated rates of horizontal ground-water velocity in the sand and gravel range from 0.2 to 0.6 m/d. These estimates are based on an average hydraulic gradient of 1.5 m/km, a horizontal hydraulic conductivity of 60 to 120 m/d, and a porosity of 30 to 40 percent (LeBlanc, 1984c).

SEWAGE PLUME

Disposal of treated sewage onto infiltration sand beds at Otis Air Base (fig. 1) since 1936 has created a plume of contaminated ground water (LeBlanc, 1984 b, c) that is 0.8 to 1.1 km (kilometers) wide, 23 m thick, and more than 4.5 km long (fig. 1). The plume moves to the south in the direction of ground-water flow and is overlain by up to 15 m of uncontaminated ground water derived from precipitation that recharges the aquifer. Part of the plume discharges to Ashumet Pond (fig. 1), which is located about 500 m from the disposal beds.

The plume of sewage-contaminated ground water is characterized by elevated concentrations of dissolved solids, boron, chloride, sodium, phosphorus, ammonium, nitrate, detergents (LeBlanc, 1984c), and volatile organic compounds (VOC), including dichloroethylene, trichloroethylene, and tetrachloroethylene (Thurman and others, 1984; Barber and others, 1988). Boron, chloride, and sodium appear to be conservative and nonreactive constituents that are attenuated primarily by hydrodynamic dispersion. Phosphorus movement is greatly retarded by adsorption onto the sediments (LeBlanc, 1984c); colloidal precipitation of iron-phosphate compounds also may affect phosphorus transport near the disposal beds (Gschwend and Reynolds, 1987; Backhus and Gschwend, 1990; Backhus and others, 1993).

Ammonium is the predominant nitrogen species in the center of the plume within 1.5 km of the disposal beds (LeBlanc, 1984c). The distribution of ammonium is caused, in part, by adsorption onto the aquifer sediments, which retards the movement of ammonium (Ceazan and others, 1989). Beyond 1.5 km, the predominant nitrogen species changes to nitrate. Nitrate cannot be detected in the center of the plume immediately downgradient of the disposal beds, even though nitrate concentrations in the sewage effluent are as high as 16 mg/L (milligrams per liter) (as nitrogen (N)), because microbially mediated denitrification has converted the nitrate to nitrogen gas (Smith and others, 1991b).

Detergent (methylene-blue-active substances) concentrations exceed 0.5 mg/L from 0.9 to 3.0 km downgradient from the disposal beds. This distribution of detergents reflects the use of nonbiodegradable detergents during 1946-64 (LeBlanc, 1984c; Thurman and others, 1986; Thurman and others, 1987). Although more than 90 percent of the biodegradable detergents are presently removed by the wastewater-treatment facility, the remaining detergents which enter the aquifer degrade slowly and are detected as far as 1.5 km from the disposal site (Field and others, 1992a, 1992b).

Elevated VOC concentrations are present in two zones in the study area. The source of the VOC zone immediately downgradient from the disposal beds may be unrelated to the sewage disposal because the VOC's are found beneath the sewage plume. However, the VOC zone 500 to 2,600 m downgradient from the disposal beds is thought to originate from the sewage-treatment facility because the VOC's are found within the sewage plume (Thurman and others, 1984; Barber and others, 1988; Barber and others,
VOC concentrations in the downgradient zone exceed 50 micrograms per liter, which suggests that these compounds are mobile and not readily degraded in the sandy aquifer (Barber, 1988; Barber and others, 1988).

Bacterial population counts as large as 2 x 10^6/mL (per milliliter) are found in ground water near the disposal site; these counts decrease by an order of magnitude more than 1 km from the beds (Harvey and others, 1984). These numbers appear to correlate with the availability of degradable organic compounds; concentrations of dissolved organic carbon (DOC) decrease from 12 mg/L to less than 2 mg/L over the same distance (Thurman and others, 1986; Harvey and Barber, 1992; Metge and others, 1993). Assays of microbial activity have been made for ground water and aquifer sediments because more than 90 percent of the bacteria are attached to silt- and clay-sized particles (Harvey and George, 1987; Smith and Duff, 1988). These assays show that rates of microbially mediated denitrification are greatest in water and sediment collected from a 1- to 2-m-thick zone near the top of the plume. The presence of the thin zone of elevated microbial activity demonstrates the need for sampling ground water and aquifer sediments at closely spaced vertical intervals (Smith and others, 1991a.)

RESEARCH ON TRANSPORT PROCESSES

Past research efforts at the Cape Cod Toxic-Substances Hydrology research site have focused on defining and describing the extent of ground-water contamination in the sewage plume. Current research at the site includes efforts to characterize specific physical, chemical, and microbiological processes affecting the transport and fate of solutes and microorganisms in the aquifer. These processes are characterized using small-scale laboratory experiments, such as batch and column tests; intermediate-scale field experiments, such as natural-gradient tracer tests with transport distances of 1 to 280 m; and large-scale investigations of the sewage plume.

Physical Transport

A major objective at the Cape Cod site has been to relate the dispersion of solutes to the heterogeneity of the aquifer's hydraulic properties. A direct measure of the dispersion of solutes in the aquifer was obtained by a spatial-moments analysis of a large-scale natural-gradient tracer test (fig. 1) conducted during 1985-88 (LeBlanc and others, 1991; Garabedian and others, 1991). Bromide, a nonreactive tracer, was monitored with a three-dimensional array of about 10,000 sampling points in an abandoned gravel pit as the tracer moved 280 m through the aquifer. The spatial-moments analysis indicates that the dispersivity is about 1.0 m in the direction of flow (longitudinal), about 0.02 m in the transverse horizontal direction, and about 0.002 m in the transverse vertical direction (Garabedian and others, 1991). The extremely detailed bromide distributions were also used by Knopman and others (1991) to test various sampling-design strategies.

Application of a numerical model of density-dependent flow (LeBlanc and Celia, 1996) to the large-scale natural-gradient tracer test shows that the density difference between the ambient ground water and the tracer solution was sufficient to cause part of the downward movement of the tracer cloud observed during the test. The density-induced downward movement was most important during the first 37 days of transport when the density difference was greatest. Intermittent recharge from precipitation also caused part of the downward movement.

Hess and others (1992) used the theoretical stochastic transport equations of Gelhar and Axness (1983) to estimate aquifer macrodispersivity at the Cape Cod site from the statistical properties of the hydraulic-conductivity distribution. The statistics were obtained from the analysis of nearly 1,500 measurements of hydraulic conductivity that were made using borehole-flowmeter tests and permeameter analyses of cores (Wolf and others, 1991) near the location of the large-scale tracer test. The range of estimated longitudinal macrodispersivity is 0.35 to 0.78 m; this range is similar to the longitudinal dispersivity observed in the large-scale tracer test.

Reilly and LeBlanc (1996) conducted a well-purging experiment to test the hypothesis that the spatial heterogeneity of hydraulic conductivity and water chemistry in the aquifer near a well can cause the chemical composition of the water sampled from the well to vary temporally as the well is pumped. They observed temporal trends in specific conductance and concentrations of ferrous iron and calcium during well purging which agree with the
hypothesis that the trends are due to flow and solute transport in the heterogeneous aquifer in the immediate vicinity of the well and not to the purging of standing water in the well. Morin and others (1988) used borehole geophysical logs to demonstrate that disturbance of the formation during drilling can affect the spatial heterogeneity of hydraulic conductivity adjacent to the well.

In addition to the above efforts to characterize aquifer properties and their effects on flow and solute transport at spatial scales of 1 to 280 m, recent efforts also have focused on large-scale characterization of the aquifer. Moench and others (1996) conducted an aquifer test at a partially penetrating well in the sand and gravel aquifer near the site of the large-scale natural-gradient tracer test and analyzed the water-level-drawdown data by type-curve matching. The analysis indicates that the horizontal hydraulic conductivity is 105 m/d and that the ratio of vertical to horizontal hydraulic conductivity is about 1:2, values that are consistent with estimates obtained from a stochastic analysis of detailed measurements of hydraulic conductivity made at the same site (Hess and others, 1992).

Masterson and Walter (1996) developed a preliminary regional-scale ground-water-flow model of western Cape Cod and used the model to examine the pathlines of contaminants emanating from the sewage-disposal beds. Modifications to aquifer properties used in the model resulted in similar simulated hydraulic-head distributions and rates of ground-water discharge to streams, but markedly different contaminant pathlines. An accurate representation of the regional hydrogeologic framework, especially the thickness and hydraulic conductivity of the fine sand and silt beneath the permeable sand and gravel, was needed to simulate the observed path of the sewage plume accurately, even though the simulated heads and discharge rates were insensitive to these aquifer properties in the model.

### Chemical Processes

More than 30 tracer tests have been conducted to determine geochemical controls on reactive transport in the heterogeneous aquifer. Two reactive tracers, lithium and molybdate, were monitored as part of the 1985-88 large-scale natural-gradient tracer test and were found to be significantly retarded relative to bromide (LeBlanc and others, 1991). Adsorption of lithium, a cation, occurs on the mineral surfaces and, more significantly, inside the weathered grains (Wood and others, 1990), where adsorption is controlled by diffusion into pores inside the grains. The diffusion-controlled adsorption resulted in a skewed distribution of lithium, with higher concentrations near the leading edge of the solute cloud and lower concentrations in the trailing edge. Adsorption of molybdate (an oxyanion of molybdenum) was affected during the tracer test by the presence of the sewage plume, which caused variations with depth in pH and concentrations of phosphate, an oxyanion that competes with molybdate for adsorption sites (Stollenwerk and Kipp, 1990).

The effect of hydrologic and geochemical processes on metal-ion transport was evaluated in a series of laboratory experiments and small-scale tracer tests conducted at the Cape Cod site (Davis and others, 1996). The results of 12 natural-gradient tracer tests performed during 1988-92 using zinc, nickel, chromium, selenium, and ethylenediaminetetraacetic acid (EDTA) show that adsorption-desorption, aqueous-complexation, and oxidation-reduction reactions affect the transport of the reactive metals during transport through the uncontaminated, oxic zone and the sewage-contaminated, mildly reducing zone of the aquifer. The transport of chromium showed a marked dependence on its speciation and the chemical composition of the ambient ground water (Kent and others, 1994; Anderson and others, 1994). The results of the laboratory experiments and small-scale tracer tests were used to design a natural-gradient tracer test, which began in April 1993, to examine transport of a complex mixture of reactive metal ions (Davis and others, 1996). The large-scale test, in which eight tracers (bromide, chromium, zinc, copper, lead, nickel, potassium, and EDTA) were dissolved in 10,000 liters of water and injected as a pulse into the aquifer, will involve detailed observation of the tracer cloud as it moves as much as 200 m through the sand and gravel.

The geochemical properties of the aquifer sediments that control metal-ion transport are being investigated in conjunction with the tracer experiments to determine their potential use as indicators of the spatial variability of metal adsorption in the aquifer. Fuller and others (1996) show that lead and zinc are adsorbed primarily by iron- and aluminum-oxide coatings on the surfaces of the quartz grains. The amount of adsorption, which varies by a
factor of two to four, is related to the amount of iron and aluminum that can be dissolved from the aquifer material by partial chemical extraction when the amounts that can be adsorbed and dissolved are normalized to surface area.

Hess and others (1996) compared the spatial variability of metal-ion adsorption to estimates of hydraulic conductivity based on the results of laboratory experiments on 375 sediment samples from 14 boreholes at the tracer-test site. Zinc and lead adsorption were measured in batch experiments (Fuller and others, 1996), whereas hydraulic conductivity was estimated from grain-size distributions. There is a statistically significant, but weak, negative correlation between lead adsorption and hydraulic conductivity. Garabedian and others (1988) used a stochastic analysis to demonstrate that a negative correlation similar to that observed for lead adsorption increases the apparent dispersion of a sorbing solute.

Geochemical heterogeneity of the sand and gravel also affects the sorption of organic compounds. Barber and others (1992a) and Barber (1994) showed that sorption of chlorobenzenes to the Cape Cod sediments increases as the particle size decreases because the fine-grained sediments have a larger total surface area, a greater abundance of magnetic minerals, and higher concentrations of sediment organic carbon than coarse-grained sediments in the aquifer.

Adsorption of metals ions in the sewage plume (Rea and others, 1996) has prevented significant transport of the metals zinc, copper, and lead away from the sewage-disposal beds. The extent of adsorption is affected by vertical gradients of pH characteristic of the transition between the sewage-contaminated ground water and the uncontaminated ground water that overlies the plume (Smith and others, 1991a).

Adsorption to the aquifer sediments also has retarded the transport of phosphate in the sewage plume (Rea and others, 1996). Phosphate concentrations in the ground water near the disposal beds are similar to those measured in the treated sewage. Because phosphate sorbs strongly to the sediments, the high concentrations in ground water indicate the presence of a large reservoir of phosphate sorbed to the aquifer sediments. The reservoir of sorbed phosphate may be remobilized after sewage disposal is stopped, as planned in late 1995, and some phosphorus may be transported in ground water that discharges to Ashumet Pond (fig. 1). A series of laboratory column experiments (Stollenwerk, 1996) indicates that the phosphate may desorb slowly as the sewage plume is flushed naturally from the aquifer. About 160 pore volumes were eluted from the column before phosphate concentrations decreased to levels generally considered by limnologists not to cause eutrophication of lakes (about 0.05 mg/L).

The above studies indicate that the geochemical environment greatly affects the transport and fate of reactive contaminants. An earlier study (Lee, 1991) had shown that the principal process affecting the ambient chemistry of the shallow, uncontaminated ground water in the study area is the carbon-dioxide-controlled hydrolysis of sodium feldspar. Lee (1996) measured carbon dioxide concentrations in soil gases from the unsaturated zone at 20 sites. The measurements show that carbon dioxide concentrations vary significantly from site to site, depending on land use, and may cause related variations in ambient water chemistry over the study area.

### Microbiological Processes

The microbial populations and their activity and transport in the aquifer have been characterized by several techniques. The use of small-scale tracer tests to measure microbial activity directly in the aquifer at a site where denitrification is occurring was tested using methane and hexafluoroethane as tracers (Smith and others, 1991c). These dissolved gases were transported without retardation, but concentrations of methane apparently decreased because of biodegradation. Acetylene, a dissolved gas, was subsequently used as a tracer because it inhibits the final step in the denitrification process and allows in situ measurement of the denitrification rate (Brooks and others, 1996). The measured rates of denitrification were generally lower than those reported for aquatic sediments or measured in the laboratory with sediments from the Cape Cod site, suggesting that laboratory methods may overestimate the rate of denitrification in the aquifer. Brooks and others (1992) reported that measurements of denitrification in the laboratory may also be biased when chloramphenicol, a common amendment in microbial-activity assays, is used.

The denitrification studies suggest that biodegradation can remove contaminants from
aquifers. Smith and others (1994) identified several strains of bacteria that consume nitrate when hydrogen or formate are added to sediment samples collected from the zone of active denitrification in the sewage plume. The degradation of trichloroethylene was observed in sediment from the Cape Cod site that had been inoculated with genetically engineered bacteria (Krumme and others, 1993). Survival of the parental strain of the genetically engineered bacteria for more than 100 days after it had been injected into the aquifer indicates that laboratory strains of bacteria can survive for extended periods of time in the subsurface and may be effective agents for bioremediation (Krumme and others, 1994; Thiem and others, 1994).

Tracer tests conducted at the Cape Cod site show that bacteria can be transported significant distances through the aquifer (Harvey and others, 1989). In one test, the bacteria moved about 7 m at the same rate as a nonreactive tracer, bromide, under a natural hydraulic gradient, although the concentrations of bacteria declined relative to the concentration of bromide. Adsorption and differential size exclusion (filtering) of bacteria from small pores can vary significantly in the heterogeneous aquifer sediments and greatly affect bacterial transport and attenuation (Harvey and Garabedian, 1991, 1992; Harvey and others, 1993). Geochemical conditions, such as the pH of the ground water and the presence of oxyhydroxide coatings on the sediment grains, also affect the transport of bacteria (Scholl and Havey, 1992). In column experiments using sediment from the Cape Cod site, an increase in pH from 5.8 to 7.9 resulted in a 70 percent decrease in bacterial attachment (Metge and others, 1996). Bacterial attachment was also affected by changes in the amount and type of DOC and the ionic strength and divalent-anion concentration in the ground water. The pH also affects the attachment of bacteriophage (bacteria-specific viruses) to the Cape Cod sediments (Kinoshita and others, 1993).

A survey of the abundance of protozoa in the sewage plume showed that their abundance typically varies from 10,000 to 100,000 per gram of sediment and is directly related to the concentration of DOC in the ground water (Kinner and Harvey, 1996). The protozoa consist largely of small (2-3 micrometer-long) flagellates. It had been assumed that the role of protozoa in the subsurface ecosystem would be similar to their role in other environments—that is, as predators of bacteria. But their small size and correlation with the concentration of DOC suggests that they feed directly on the organic compounds.

The transport of protozoa was examined by means of several small-scale, natural-gradient tracer tests (Harvey and others, 1996). The retardation and immobilization of the protozoa were several orders of magnitude greater than the retardation and immobilization of bacteria in the same experiments. The high degree of immobilization and retardation may be related to the surface chemistry of the protozoa and not to their size.

SUMMARY

Past research efforts at the Cape Cod Toxic-Substances Hydrology research site have focused on defining and describing the extent of ground-water contamination in a sewage plume emanating from the Otis Air Base sewage-treatment facility on Cape Cod, Mass. Current research at the site includes efforts to characterize specific physical, chemical, and microbiological processes affecting the transport and fate of solutes and bacteria in the aquifer. These processes are characterized by means of small-scale laboratory experiments, such as batch and column tests; intermediate-scale field experiments, such as natural-gradient tracer tests with transport distances of 1 to 280 m; and large-scale investigations of the sewage plume.

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The Transport of Inorganic Contaminants in a Sewage Plume in the Cape Cod Aquifer, Massachusetts

By Brigid A. Rea¹, Douglas B. Kent², Linda C. D. Anderson², James A. Davis², and Denis R. LeBlanc³

Abstract

The active and abandoned sewage-disposal beds at the Massachusetts Military Reservation sewage-treatment plant are a major source of inorganic contaminants, such as zinc, copper, and phosphate, in the Cape Cod aquifer, Massachusetts. The distribution and mobilities of these chemical constituents around the sewage-treatment plant are strongly affected by geochemical processes; extensive adsorption results in confinement of the most intensive concentrations to the near-source region, including currently used and abandoned disposal facilities. Beyond the disposal facilities, zinc and copper movement continues to be controlled by sorption processes. Zinc and copper contamination was present at the same depths, although copper concentrations were much lower than those of zinc. Phosphate concentrations were high in the suboxic zone near the source and are controlled by adsorption to sediments. Phosphate concentrations in the anoxic zone were much lower and likely are controlled by ferrous phosphate solubility.

INTRODUCTION

Inorganic contaminants in the subsurface travel at widely variable rates. The mobility of contaminants is strongly dependent on their speciation, aquifer pH, redox reactions, and mineral composition of the aquifer material (Davis and Kent, 1990; Sposito, 1984). In this paper, we report on the processes that affect the distribution of sewage-derived phosphate, zinc (Zn) and copper (Cu) in the ground water near the sewage-effluent disposal beds (also termed “sand beds”) at the U.S. Geological Survey Cape Cod Toxic Substance Hydrology Research site (fig. 1). A contrast in relative rates of transport is made between the two cations (Zn and Cu) and phosphate (an oxyanion) on the basis of expected ion-adsorption phenomena. Cation adsorption generally increases with an increase in pH, whereas anion adsorption decreases with an increase in pH.

In a previous paper (Rea and others, 1991), we described a small plume of dissolved Zn in a transition zone between pristine recharge water (infiltrated precipitation) and suboxic sewage-contaminated water; the 2-m-thick plume extended approximately 350 m downgradient from the sewage disposal beds (fig. 1). We postulated that the mobility of Zn was controlled by sorption reactions, which are affected by pH and Zn concentration. Concentrations of dissolved Zn in equilibrium with sorbed Zn on the aquifer solids decrease with increasing pH; above pH 6.0, Zn concentrations in equilibrium with sorbed Zn are often below detection (Rea and others, 1991). At constant pH, the amount of Zn sorbed increases with increasing Zn concentration until the maximum sorptive capacity is achieved (Davis and Kent, 1990; Sposito, 1984). In the sewage-contaminated zone, Zn can move only after the available sorption sites are saturated with sorbed Zn and other metals that compete for sorption sites. In the transition region, decreased pH, resulting from the mixing with pristine ground water, enhances Zn mobility enough to cause the observed Zn plume (Rea and others, 1991).

Zn in the sewage effluent is likely derived from pipe corrosion (Foerstner and Van Lierde, 1983). This led us to look for elevated concentrations of other metal ions, in particular Cu and lead (Pb). Both Cu and Pb adsorb to minerals more strongly than does Zn (Sposito, 1984; Dzomback and Morel, 1990). Consequently, contamination of the aquifer by these metals is expected to be limited to an area near the source; however, mobilization of these metals could occur in response to changes in the ground-water chemistry.

Phosphate contamination has been reported previously in the Cape Cod aquifer (LeBlanc, 1984; Gschwend and Reynolds, 1987). Recently, local communities have become concerned that the contribution of phosphate from the Massachusetts Military Reservation (MMR) sewage-treatment plant may be
responsible for algal blooms, fish kills, and a general decline in the water quality (eutrophication) of Ashu- met Pond (K-V Associates, Inc. and IEP, Inc., 1991). An improved understanding of the geochemical processes affecting the transport of phosphate in the aquifer and of the interaction of the sewage plume with Ashumet Pond is required to evaluate remediation strategies.

In addition to studying the transport of these chemical constituents, we examined the possible sources of contamination and their potential effect on ground-water quality.

SITE DESCRIPTION

Discharge of secondary-treated sewage effluent from the MMR sewage-treatment plant into a sand and gravel aquifer on Cape Cod, Massachusetts (fig. 1) has generated distinct zones of ground-water chemistry separated by steep vertical gradients in chemical composition (LeBlanc, 1984; Smith and others, 1991; Davis and others, 1991; Kent and others, 1993). Pristine ground water (that is, water derived from precipitation) overlies the sewage plume. The pristine ground water is oxic, has a pH of 4.5 to 5.5, and low concentrations of dissolved salts (Davis and others, 1991). The sewage plume consists of a suboxic rim and an anoxic core (Smith and Duff, 1988). The suboxic rim is characterized by dissolved oxygen (DO) concentrations less than 5 μM and mildly reducing conditions, a pH of 5.5 to 6.5, and moderate concentrations of dissolved salts (Davis and others, 1991; Kent and others, 1993). The anoxic core has ferrous iron (Fe^{2+}) and ammonium concentrations greater than 300 μM. Values of pH and dissolved salt concentrations in the anoxic core are similar to those in the suboxic zone (Gschwend and Reynolds, 1987; Smith and Duff, 1988; Kent and others, 1993).

METHODS

Ground-water samples were collected from a number of multilevel samplers (MLS) and clusters of observation wells (Smith and others, 1991; LeBlanc and others, 1991) around the MMR sewage-treatment plant in September, 1992 (fig. 1, table 1). The DO concentration and pH of the samples were measured at each site in the field (Davis and others, 1993).

Table 1. Description of sampling sites

<table>
<thead>
<tr>
<th>Site number and descriptor</th>
<th>Well type</th>
<th>Description of location</th>
</tr>
</thead>
<tbody>
<tr>
<td>S318 (Active sand beds)</td>
<td>Multilevel sampler and observation well&lt;sup&gt;1&lt;/sup&gt;</td>
<td>Secondarily-treated sewage effluent currently disposed in this location</td>
</tr>
<tr>
<td>S438 (Abandoned sand beds)</td>
<td>Observation well</td>
<td>Disposal of treated sewage effluent ceased in this location in 1984</td>
</tr>
<tr>
<td>S314</td>
<td>Observation well</td>
<td>Less than 10 m downgradient of site S318 in the active sand beds</td>
</tr>
<tr>
<td>F230</td>
<td>Cluster of observation wells</td>
<td>Approximately 100 m downgradient of site S318 in the active sand beds</td>
</tr>
<tr>
<td>S434 (Inactive sludge drying pad)</td>
<td>Cluster of observation wells</td>
<td>Sludge from treatment plant dried on these pads prior to disposal in land fill</td>
</tr>
</tbody>
</table>

<sup>1</sup> All observation wells: 5.1 cm diameter with 0.6-m-long screens.
Ground-water samples were filtered (0.4 μm), preserved by acidification to pH 2 (with trace-metal grade HCl), and shipped overnight to Menlo Park, California, for analysis. These samples were analyzed for metals, boron, and phosphate by inductively coupled argon-plasma spectrometry. Some samples were analyzed in the field for phosphate using the standard colorimetric method (Franson, 1985), which is sensitive only to monomeric species. The difference in phosphate concentration determined by the two methods differed by an average of less than 1 percent (r² of 0.997), except at the lowest concentrations where the colorimetric method has a large uncertainty. This showed that dissolved phosphate was present as monomeric species, often called "orthophosphate."

RESULTS

Ground-water Chemistry

The ground-water chemistry at sites near the sewage-treatment plant depends on the historical use of the overlying sediments and the proximity of the sites to the source of contamination (table 1). At the active sewage-disposal sand beds, the concentration of DO in the ground water decreased from the water table (13.9 m above sea level and approximately 11.6 m below land surface) to a depth of about 9.5 m above sea level; all DO measurements from altitudes below 9.5 m were near zero (site S318, fig. 2). Dissolved boron (B) concentrations exceeded 20 μM in all depths examined (B is used as an indicator of sewage-contaminated water (LeBlanc, 1984)). The presence of B showed that sewage-contaminated ground water extended upward to the water table. Ground water at this site consistently has significant concentrations of DO in the sewage-contaminated zone (Smith and others, 1991; Rea and others, 1991). The concentration of sewage-derived elements in the ground water at an abandoned sand bed fell within the ranges of those in the ground water beneath the active bed.

The vertical zonation of ground-water chemistry typical of sewage plume was much better developed at well site F230 than at the active sand beds; site F230 is approximately 100 m downgradient from the active sand beds (fig. 3; table 1). The presence of some B (and phosphate) just below the water table indicates that ground water at this depth is a mixture of sewage-contaminated and pristine ground water because both B and phosphate are below detection in pristine ground water. In contrast with the active sand beds (site S318), dissolved oxygen concentrations at site F230 were low throughout the sewage-contaminated zone (where B concentrations exceeded 10 μM; see fig. 3). Ground water from the sampling point near sea level was anoxic and had an Fe²⁺ concentration of 23 μM.

High concentrations of DO in the ground water from the well cluster in the inactive sludge-drying pad indicate that the chemistry of the ground water at the site is similar to that of pristine ground water (table 2). Concentrations of phosphate and B were very low throughout this well-oxygenated profile.

Distribution of Zinc

Zn concentrations in the active sewage disposal beds agree well with Zn concentrations in ground-water samples collected in August 1990 by Rea and others (1991); the uppermost ground-water sample had a Zn concentration of almost 2.3 μM at each sampling (fig. 2). The concentration of dissolved Zn generally decreased with depth but remained above the concentrations found in the pristine (background) ground water. Ground water at the water table in the abandoned sand beds also contained concentrations of Zn well above those in pristine ground water (table 2). At sites 10 and 100 m downgradient from the abandoned sand beds (site S314 and site F230, respectively), dissolved Zn concentrations were high in comparison with those observed beneath the active sand beds (site S318) (fig. 3, table 2). Some contamination from the submersible pump used to withdraw water samples from the screened wells may have occurred. However, good agreement between Zn concentrations in ground water collected with submersible pump and peristaltic pump (in which the water never contacts metal) were obtained at the active sand beds (table 1, fig. 2). This point requires further investigation.

Concentrations of Zn at the inactive sludge-drying pad, which is upgradient of the disposal beds, decreased with depth (table 2). This indicates some contamination of the sediments from past sludge-drying practices. Current practices involve drying sludge in lined beds.
Figure 2. Vertical profiles of ground-water chemistry in one of the active sewage disposal beds (site S318). (A) Dissolved orthophosphate concentration (●) and pH (□) as a function of depth. (B) Dissolved zinc (△) and dissolved copper (▲) as a function of depth. (C) Dissolved boron (○) and dissolved oxygen (●) as a function of depth.

Figure 3. Vertical profiles of ground-water chemistry of site F230, approximately 100 meters downgradient of the active sewage disposal beds. (A) Dissolved orthophosphate concentration (●) and pH (□) as a function of depth. (B) Dissolved zinc (△) and dissolved copper (▲) as a function of depth. (C) Dissolved boron (○) and dissolved oxygen (●) as a function of depth. Error bars on sample points show screened interval on well.
Table 2. Chemical characteristics of ground water in the vicinity of MMR sewage-treatment plant
[Altitude measured in meters; all concentrations are units of micromolar except pH, which is on National Bureau of Standards pH scale; <, below detection limit of instrument]

<table>
<thead>
<tr>
<th>Location and well site</th>
<th>Altitude above sea level</th>
<th>Phosphate</th>
<th>Zinc</th>
<th>Copper</th>
<th>Boron</th>
<th>Dissolved Oxygen</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inactive sludge-drying pad</td>
<td>S434-13</td>
<td>13.21</td>
<td>4.20</td>
<td>2.78</td>
<td>0.26</td>
<td>1.5</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>S434-25</td>
<td>10.46</td>
<td>18.1</td>
<td>0.61</td>
<td>&lt;.06</td>
<td>0.61</td>
<td>170</td>
</tr>
<tr>
<td></td>
<td>S434-75</td>
<td>-4.89</td>
<td>&lt;3.2</td>
<td>&lt;0.15</td>
<td>&lt;0.06</td>
<td>&lt;0.06</td>
<td>320</td>
</tr>
<tr>
<td>Active sand bed</td>
<td>S318-36</td>
<td>10.24</td>
<td>177</td>
<td>.69</td>
<td>.84</td>
<td>31.5</td>
<td>16</td>
</tr>
<tr>
<td>Downgradient of active sand bed</td>
<td>S314-35</td>
<td>13.93</td>
<td>121</td>
<td>5.31</td>
<td>1.17</td>
<td>27.0</td>
<td>63</td>
</tr>
<tr>
<td>Abandoned sand bed</td>
<td>S438-41</td>
<td>12.52</td>
<td>116</td>
<td>1.30</td>
<td>1.02</td>
<td>30.1</td>
<td>94</td>
</tr>
</tbody>
</table>

1Water table at 13.9 m above sea level.

Distribution of Copper and Lead

Dissolved Cu concentrations beneath the active sand beds were 0.5 to 1 μM throughout the vertical profile below the water table (fig. 2). Similar values for Cu were found in the ground water beneath the abandoned sand beds and 10 m downgradient from the sewage-disposal beds (table 2). At site F230, concentrations of Cu were only slightly greater than background Cu concentrations in the aquifer.

Concentrations of dissolved Pb were below the detection limit (less than 0.1 μM) in all samples.

Distribution of Phosphate

High concentrations of phosphate were observed in the ground water at all depths beneath the active sand beds (fig. 2, table 1). Phosphate concentrations in the ground water at this site were similar to those measured in a sample of the effluent (170 μM). Phosphate adsorbs strongly to minerals, but adsorption decreases with increasing pH (Sposito, 1984; Sigg and Stumm, 1980; Goldberg and Sposito, 1986a, 1986b). Thus, we expect that the observed concentrations of phosphate also are supported by a large reservoir of adsorbed phosphate. A similar reservoir must exist in the abandoned sand beds because a high concentration of phosphate still was detected in the ground water (table 2) nearly 10 years after sewage disposal at that site had ended.

A distinct phosphate profile was observed in the ground water at site F230 (fig. 2). The phosphate concentration of the nearly pristine ground water near the water table was low; in the suboxic zone, high concentrations of phosphate, similar to those in the active sand beds, were observed. Low phosphate concentrations were measured in the anoxic ground water, similar to those reported earlier (Gschwend and Reynolds, 1987).

DISCUSSION

The results of this study provide insight into the development of the vertical zonation of ground-water chemistry that characterizes the sewage plume. High concentrations of DO introduced to the upper region of the sewage-contaminated zone during infiltration of the sewage effluent (fig. 2) decreased during the first 100 m of transport to concentrations characteristic of the suboxic zone (fig. 3). Low concentrations of DO
affect the redox conditions of the aquifer which, in turn, can cause changes in the mobility of various ions.

Zn and Cu are strongly adsorbed to sediments at the pH values observed at the sewage-disposal beds (Rea and others, 1991; Coston and others, 1992) indicating that a large reservoir of these elements must be adsorbed to the sediments. Lower concentrations and less movement of Cu downgradient compared to that of Zn are consistent with the greater adsorptivity of Cu (although complexation with organic material could enhance Cu mobility). The absence of dissolved Pb may result from the even greater adsorptivity of Pb compared to that of Cu at the pH in the ground water beneath the sewage-disposal beds (Davis and Kent, 1990; Sposito, 1984). Alternatively, contamination by to Pb may be less extreme than that by Cu. Extractions of core material collected from the vicinity of the sewage-treatment plant, currently underway, will enable us to quantify the concentration of sorbed metals with improved accuracy. The contribution of metals from abandoned facilities (effluent-disposal beds and sludge-drying pads) is likely; leakage of effluent from the sewage treatment plant also is possible. Further investigation is required to determine all sources of input.

Phosphate transport in the suboxic zone probably is controlled by adsorption. In the anoxic zone, phosphate transport is closely linked to the availability of Fe$^{2+}$ and the solubility of Fe$^{2+}$-phosphate minerals (Gschwend and Reynolds, 1987). Extractions of core material will help evaluate the geochemical processes affecting phosphate mobility. Additional sampling downgradient is required to understand geochemical processes affecting phosphate transport.

### SUMMARY AND CONCLUSIONS

The Cape Cod aquifer has been contaminated with Zn, Cu, and phosphate by a sewage plume emanating from the MMR sewage-treatment facility. As a result of the extensive adsorption of these solutes to aquifer solids under the prevailing chemical conditions of the ground water, the greatest amount of contamination is confined to a region near the source of contamination, including abandoned facilities. The geochemical processes controlling the mobility of Zn, Cu, and phosphate are strongly coupled to those processes that give rise to the steep vertical chemical gradients in the sewage plume. In the suboxic zone, mobility is controlled by adsorption processes, which depend on pH, the concentration of the adsorbing species, and the concentrations of other solutes that compete for adsorption sites. The greater adsorptivity of Cu compared to that of Zn results in the observed decreases in mobility of Cu. Phosphate mobility in the suboxic zone is controlled by adsorption. In the anoxic zone, dissolved phosphate concentrations are likely controlled by the solubility of Fe$^{2+}$ phosphate.

### REFERENCES


Potential Long-Term Effects of Phosphate Contamination in a Sand and Gravel Aquifer, Cape Cod, Massachusetts

By Kenneth G. Stollenwerk

Abstract

Phosphate in the Ashumet Valley sewage plume, located near Falmouth, Massachusetts, could increase the rate of eutrophication in Ashumet Pond. A series of column experiments has been initiated to identify the geochemical processes affecting transport of phosphate in this aquifer. The principal focus of these experiments is to determine the amount and rate of phosphate desorption from aquifer sediment after sewage disposal is stopped. The first set of column experiments simulated the oxic zone that surrounds the core of the plume. Results indicate that the sediment has a relatively high capacity to adsorb phosphate and that adsorption is kinetically controlled. The rate of desorption is slow. Approximately 160 pore volumes were eluted before the phosphate concentration decreased to levels considered not to cause eutrophication; half the phosphate was still adsorbed on the sediment. A one-dimensional solute transport code simulated the column data reasonably well; however, a kinetic term needs to be included in the model to improve accuracy.

INTRODUCTION

Part of the Ashumet Valley sewage plume from the Massachusetts Military Reservation sewage-infiltration beds is discharging to Ashumet Pond (fig. 1). Evidence of the discharge includes increased specific conductance and concentrations of boron and phosphate (PO₄) in water samples collected from wells near the pond, from minipiezometers set in the pond bottom, and from near-shore surface water (LeBlanc, 1984).

Ashumet Pond is phosphorus (P) limited. The dissolved PO₄ concentration in Ashumet Pond (1991) averages 0.32 to 0.64 μmol/L, although localized areas of higher concentration have been measured near shoreline sources (K-V Associates, 1991). Generally, PO₄ concentrations greater than 0.64 μmol/L are considered to cause eutrophication (Vollenweider, 1968). The condition of Ashumet Pond is considered to be mesotrophic with signs of eutrophication (K-V Associates, 1991). Approximately 30 percent of the current annual PO₄ input to the pond is from the sewage plume. Computer simulations predict that by the mid 1990's the sewage plume will contribute more than 70 percent of the PO₄ load to the pond (K-V Associates, 1991).

Because of the potential for eutrophication, the National Guard has decided to begin remediation efforts to prevent future discharge of PO₄ to the pond. Discharge of sewage at this site is scheduled to terminate in 1995. The National Guard is funding an investigation by the U.S. Geological Survey to obtain the hydrogeologic and geochemical information needed to evaluate methods for preventing discharge of PO₄ in the aquifer upgradient of Ashumet Pond. Objectives of this study include (1) delineation of the PO₄ plume between the sewage infiltration beds and Ashumet Pond; (2) description of ground-water flow between the sewage infiltration beds and Ashumet Pond; (3) identification of the geochemical processes affecting PO₄ transport; and (4) predict future transport of PO₄ after cessation of sewage discharge.

Phosphate in the plume is attenuated by sorption to aquifer sediment. As of the last major sampling, in 1988, the leading edge of the sewage plume was about 4.5 km from the infiltration beds, whereas the leading edge of the PO₄ plume had only traveled 0.8 km (fig. 1). The amount and rate of PO₄ released from the
Figure 1. Water-table map showing location of sewage and phosphorus plumes, 1988. Phosphorus plume is defined by dissolved concentration greater than 1 μmol/L. (Modified from LeBlanc, 1984).
sediment after sewage discharge is stopped could have a major effect on the remediation strategy. One method of evaluating the release of PO₄ from aquifer sediment is through use of laboratory column experiments designed to simulate the flow and geochemical conditions in the plume as closely as possible. Different geochemical environments exist within the aquifer as a result of mixing of freshwater recharge with the sewage plume (Smith and others, 1991). This paper describes the results from a column experiment representing the partially oxic conditions that surround the core of the plume.

METHODS

Experimental

Replicate columns, 30 cm long by 2.5 cm inside diameter, were filled with the less than 2-mm-size fraction of sediment collected from the unsaturated zone of the aquifer above the sewage plume. This size fraction accounted for 90 percent by weight of the sediment sample. Pre-sewage-plume conditions were established in each column by rinsing the sediment with several pore volumes of uncontaminated ground water (UGW) collected from the aquifer. A bromide tracer was used to estimate the dispersivity for transport simulation. After the bromide was eluted from the columns, influent was switched to sewage-contaminated ground water (SCGW) collected from the oxic part of the plume. The SCGW contained 15.8 µmol/L PO₄ and had a higher pH and dissolved solids content than did UGW (table 1). Sewage-contaminated ground water was eluted through the column until the PO₄ concentration in effluent approached the influent concentration. The influent then was changed to UGW to evaluate the rinse-out of PO₄ from the columns. Separate peristaltic pumps were used to drive the solutions through each column at a velocity of 0.4 m/d, the velocity of ground water in the aquifer (LeBlanc and others, 1991). Effluent was collected in a fraction collector.

Phosphate was analyzed by the phosphomolybdate colorimetric procedure (Fishman and Friedman, 1985). Sulfate, chloride, nitrate, nitrite, calcium, magnesium, potassium, sodium, and ammonium concentrations were analyzed by ion chromatography.

Table 1. Chemical composition of ground water used in the column experiment

<table>
<thead>
<tr>
<th>Solute</th>
<th>Uncontaminated ground water</th>
<th>Sewage-contaminated ground water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>250</td>
<td>1450</td>
</tr>
<tr>
<td>K</td>
<td>20</td>
<td>215</td>
</tr>
<tr>
<td>Ca</td>
<td>22</td>
<td>298</td>
</tr>
<tr>
<td>Mg</td>
<td>33</td>
<td>193</td>
</tr>
<tr>
<td>Cl</td>
<td>353</td>
<td>874</td>
</tr>
<tr>
<td>SO₄</td>
<td>31</td>
<td>323</td>
</tr>
<tr>
<td>NO₃</td>
<td>&lt;</td>
<td>758</td>
</tr>
<tr>
<td>HCO₃</td>
<td>98</td>
<td>492</td>
</tr>
<tr>
<td>PO₄</td>
<td>&lt;</td>
<td>15.8</td>
</tr>
<tr>
<td>pH</td>
<td>5.6</td>
<td>7.2</td>
</tr>
</tbody>
</table>

1Laboratory measured pH immediately after receiving sample was 6.3. Degassing of CO₂ caused pH increase to 7.2. No attempt was made to readjust pH for column experiments.

Solute Transport Model

The solute transport code HYTEQ (Kool, 1990) was used to simulate the reaction and transport of PO₄ in the column experiment. HYTEQ is a coupling of the HYDRUS one-dimensional solute-transport code (Kool and van Genuchten, 1990) and the MINTEQA2 geochemical speciation code (Allison and others, 1990). MINTEQA2 contains the diffuse-layer surface-complexation model that was used to simulate PO₄ sorption. Input parameters for the diffuse-layer model are listed in table 2. The concentration of sorption sites was determined by potentiometric titration of sediment with hydrogen ion (H⁺) to a pH of 3.5. Equilibrium constants for the three phosphate reactions represent best fits to sorption data from batch experiments, which were conducted under the same chemical conditions used in the column experiments.

EXPERIMENTAL RESULTS

Phosphate was completely removed from the first 45 pore volumes of SCGW (fig. 2). A rapid increase in concentration was observed initially, followed by a much slower approach to complete breakthrough. Breakthrough curves for both columns were similar for the first 120 pore volumes. The greater concentration of PO₄ in column 2 between pore volumes 65 and 80 reflects a period of time when
Table 2. Surface-complexation model parameters.

<table>
<thead>
<tr>
<th>[FeOH$^0$, neutral charged reactive surface site; LogK$^\text{int}$, log of the intrinsic complexation constant]</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Sediment properties</strong></td>
</tr>
<tr>
<td>Sediment concentration - 4,600 grams per liter</td>
</tr>
<tr>
<td>Surface area - 0.33 square meters per gram</td>
</tr>
<tr>
<td>Concentration of complexation sites - 6,400 μmol/L</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Surface complexation reactions</th>
<th>LogK$^{\text{int}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) FeOH$^0$ + H$^+$ = FeOH$_2^+$</td>
<td>6.1</td>
</tr>
<tr>
<td>(2) FeOH$^0$ = FeO$^-$ + H$^+$</td>
<td>-7.3</td>
</tr>
<tr>
<td>(3) FeOH$^0$ + 3H$^+$ + PO$_4^{3-}$ = FeH$_2$PO$_4^0$ + H$_2$O</td>
<td>27.8</td>
</tr>
<tr>
<td>(4) FeOH$^0$ + 2H$^+$ + PO$_4^{3-}$ = FeHPO$_4^-$ + H$_2$O</td>
<td>21.6</td>
</tr>
<tr>
<td>(5) FeOH$^0$ + H$^+$ + PO$_4^{3-}$ = FePO$_4^{2-}$ + H$_2$O</td>
<td>16.5</td>
</tr>
</tbody>
</table>

Sediment concentration - 4,600 grams per liter
Surface area - 0.33 square meters per gram
Concentration of complexation sites - 6,400 μmol/L

the average velocity was 20 percent greater in column 2 than it was in column 1. As a result, there was less time for PO$_4$ to react with sediment in column 2. At pore volume 96, the pump driving water through column 2 began to malfunction, resulting in very slow flow velocities. Accordingly, contact time in column 2 increased, and more PO$_4$ was removed from solution than would have been had the pump not malfunctioned.

The dependence of dissolved PO$_4$ concentration on time of contact between PO$_4$ and sediment is well established (see, for example, Lijklema, 1980) and indicates a kinetic control on PO$_4$ sorption. Martin and others (1988) present convincing evidence for the formation of crystallites of graphite (Fe$_3$Mn$_2$(PO$_4$)$_2$OH$_2$) on the surface of naturally occurring goethite. They concluded that a mono-layer of PO$_4$ was rapidly adsorbed initially, followed by slow reprecipitation. The manganese (Mn) was supplied by Mn oxide impurities in the goethite. In the absence of Mn, an iron phosphate hydroxide mineral phase would form. On the other hand, Willett and others (1988) present equally convincing evidence that PO$_4$ rapidly adsorbs on all available sites on fresh hydrous ferric oxide (HFO). The rate of PO$_4$ removal from solution depended on the time required to diffuse to less accessible sites within the porous HFO structure. The different conclusions of these two studies may be a function of differences in experimental conditions and materials.

Sediment from the sewage-contaminated aquifer of this study contains amorphous to crystalline iron oxides. Both of the above mechanisms might contribute to the slow reaction of PO$_4$ observed in the columns. Although recrystallization of a PO$_4$-mineral phase has not yet been investigated, there is direct evidence for diffusion. Breakthrough curves for molybdate from previous experiments using identically prepared columns could only be simulated by a diffusion mechanism (Stollenwerk and Kipp, 1990). Whatever the mechanism, it is clear that flow velocities in column experiments should be representative of those in the aquifer to reflect the chemical and physical processes that operate in the aquifer.

Phosphate in effluent from both columns never attained the influent concentration of 15.8 μmol/L. Column 1 was switched to UGW at pore volume 115, and column 2 was switched at pore volume 160. PO$_4$ concentration in column 1 effluent was 13 μmol/L; in column 2 it was 15 μmol/L. As UGW began to elute from both columns, a brief spike in PO$_4$ concentration was observed (fig. 2). The spike could have been the result of an ion-exchange reaction, although the concentrations of other anions, such as sulfate, are less in UGW than in SCGW. Also, PO$_4$ adsorbs much more strongly than do the other anions in UGW and SCGW. The spike also could represent an initial temporary equilibrium between PO$_4$ that was loosely adsorbed to the exterior of grains and PO$_4$-free UGW.

Phosphate in effluent from both columns rapidly declined at first, then changed to an asymptotic rate of decline. Desorption in column 1 began at pore volume 115; however, the PO$_4$ concentration did not decrease to the mesotrophic/eutrophic concentration boundary of 0.64 μmol/L until pore volume 270. The shape of the desorption curve for column 2 is similar. The amount of PO$_4$ adsorbed or desorbed was quantified by keeping track of the mass balance for each aliquot collected from the column. A total of 60.8 and 63.9 μmol were sorbed by sediment in columns 1 and 2, respectively. Only about 45 percent had been desorbed by pore volume 270.
Figure 2. Breakthrough curves for phosphate from columns 1 and 2 and for pH from column 1. ($C_0$ is the initial influent concentration of phosphate = 15.8 μmol/L; * represents the pore volume where influent was switched to uncontaminated ground water containing no phosphate).

Figure 3. Experimental and simulated breakthrough curves for phosphate from column 1.
Also of interest are the pH profiles. Only the pH of effluent from column 1 is plotted in Figure 2; the pH of column 2 effluent was similar. Although influent was switched to SCGW of pH 7.2 at pore volume 0, the pH of column effluent remained near 5.6 for almost 20 pore volumes before rapidly increasing to 7.2. Apparently, the sediment has a buffering capacity for H⁺. Prior equilibration of the sediment with low-pH UGW saturated the oxide-mineral surface sites with H⁺. Desorption of H⁺ or ion exchange with cations in the SCGW maintained a low pH.

The reverse behavior was observed in the rinse-out data. When pH 5.6 water was reintroduced to the columns, pH remained high. In fact, at pore volume 275, the pH of effluent from both columns was still greater than 6. These data would seem to indicate that oxide minerals were removing H⁺ from solution. Effluent concentrations of calcium and potassium remained higher than the influent, indicating desorption, perhaps by ion exchange with H⁺. Future column experiments will be designed to address the pH question.

**SIMULATION RESULTS**

Simulation results with respect to column 1 predict that the concentration of PO₄ should rapidly increase to the influent concentration at pore volume 35 (Figure 3). This is sooner than the observed breakthrough, which began at pore volume 43. The model also underpredicted the amount of PO₄ adsorbed. The equilibrium constants for PO₄ sorption are based on data from batch experiments that were conducted for only 48 hours; thus, the time for intragranular diffusion was limited. Phosphate in the column experiment had a much longer time to diffuse to reaction sites. A kinetic term added to the transport model should improve the simulation.

Desorption of PO₄ was simulated at two pH values. The pH 7 simulation was conducted at the average measured pH of column effluent between pore volumes 120 and 280 (pH 7). This simulation predicts that PO₄ should be rapidly rinsed from the column in less than 20 pore volumes. The other simulation was conducted at the pH of the influent water (pH 5.5). Results exactly matched the actual desorption curve for PO₄ with the exception of the initial concentration spike. This match is likely fortuitous, because the actual distribution of pH in the column should be somewhere between the values used in these simulations. Near the influent end of the column, water would be expected to be in equilibrium with sediment at a pH of 5.5. Reactions would still be affecting pH at the effluent end of the column, thereby maintaining an increased pH. A more accurate simulation would take into account the changing pH within the column; however, this simulation has not yet proved feasible with the HYTEQ code. The pH could only be fixed at one value for a simulation.

**SUMMARY**

Evidence from column experiments indicates that transport of PO₄ in the oxic zone of the sewage plume should be retarded by sorption. As a result, a reservoir of sorbed PO₄ might exist between the sewage infiltration beds and Ashumet Pond. Data from column experiments indicate that a relatively large pulse of PO₄ could initially elute from the aquifer after cessation of sewage discharge. Following this spike, PO₄ will desorb and concentrations in ground water will decline slowly. Dissolved PO₄ could remain at concentrations greater than the eutrophication limit of 0.64 μmol/L for many years. Column data also indicate that approximately half the sorbed PO₄ might be irreversibly adsorbed to the sediment.

A major question that needs to be answered before considering remediation strategies concerns the amount of PO₄ currently in the aquifer. The column experiments were run until complete breakthrough of PO₄ was achieved. This condition might not represent the existing condition in the aquifer; thus, there might still be a substantial amount of sorption capacity left to intercept the PO₄ plume. Furthermore, this first set of column experiments represents the lower end of the PO₄-concentration range observed in one part of the aquifer. Additional experiments need to be done in the upper concentration range of the oxic zone, and conditions in the anoxic core of the plume need to be simulated. Finally, accurate prediction of the potential effect of PO₄ on Ashumet Pond will require simulation of the PO₄ plume in three dimensions. Initial simulations of one-dimensional column experiments are relatively accurate; however, some modifications to the model are necessary to improve accuracy.
REFERENCES


Background Aqueous Chemistry and Effects of Carbon Dioxide Variations in Recharge in Shallow Ground Water in a Glacial Outwash Aquifer, Cape Cod, Massachusetts

By Roger W. Lee

Abstract

Previous geochemical research at the Otis Air Base Site, Cape Cod, Massachusetts, determined that the principal geochemical process developing background water chemistry of shallow ground water is CO$_2$-controlled hydrolysis of sodium feldspars. Preliminary geochemical modeling, however, demonstrated that CO$_2$ sources should vary laterally over the project area. Field analyses of unsaturated zone gases showed variations in available CO$_2$ for recharge waters. These variations depend on land use and vegetative cover in the area of ground-water recharge. On the basis of measurements of CO$_2$ concentrations in unsaturated-zone gases at 20 sites, CO$_2$ dissolved in recharge water can range from about 0.035 to 1.000 millimoles per liter in the project area. The various land-use practices and local surface features in and around Otis Air Base (residential subdivisions, golf courses, large cultivated grass fields, kettle ponds, and woodlands) are associated with variations in the amount of CO$_2$ in the unsaturated zone.

INTRODUCTION

Recent research in ground water at the Otis Air Base research site, Cape Cod, Massachusetts, has focused on hydrologic, geochemical, and microbiological processes in and around a sewage plume in the glacial outwash aquifer. The initial research identified the mineral-water interactions and the role of CO$_2$ in the uncontaminated parts of the aquifer. The term “background” is used to describe ground water not contaminated by the sewage effluent. This term is not to be confused with “natural” or “pristine” ground water, which implies that ground water has not been affected by manmade changes to land use. Background water can be affected by fertilizers, septic-tank effluent, road salting, or other land uses in the area of study.

Research into the background geochemistry around Otis Air Base has been described from ground-water samples collected in 1988 and 1989 (Lee, 1991). The principal reaction determined for the shallow ground water is the CO$_2$-controlled hydrolysis of sodium feldspar. Geochemical mass-transfer models were developed using the computer code PHREEQE (Parkhurst and others, 1980) to test hypotheses of chemical evolution of shallow ground water against actual chemical data. The purpose of this paper is to characterize CO$_2$ content and seasonal variations in the unsaturated zone under different land uses. Samples for analysis of CO$_2$ concentration in gases of the unsaturated zone were collected at 20 locations for different seasons during 1991-92.

BACKGROUND AQUIFER CHEMISTRY

The chemistry of background shallow ground water is determined by the chemistry of recharge water and the interaction of that recharge water with minerals and gases in the unsaturated and saturated zones. Development of conceptual and quantitative models provides insight necessary to improve the knowledge and understanding of the geochemical processes occurring within the aquifer.

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1U.S. Geological Survey, Austin, Texas
Mineralogy

The water-table aquifer consists of 90 to 200 feet of glacial outwash sand and gravel that overlies a thick glacial till deposit (Oldale, 1969). The area of interest is in a valley (locally referred to as Ashumet Valley) that extends from the southern part of Otis Air Base to as far south as the cranberry bogs (fig. 1). The valley is bounded by sand and gravel valley ridges on the west and on the east. Ground water generally flows from north to south parallel to the axis of the valley (fig. 1). Thorough discussions of the hydrology and geology of the site are given by LeBlanc (1984) and Garabedian and LeBlanc (1991).

Minerals in the glacial outwash sands and gravels are described by Wood and others (1990) and Barber and others (1992). The sediments are well-sorted fine- to medium-grained sands with inter-spersed gravel and cobble zones. The sands contain principally quartz with small amounts of feldspar (albite, orthoclase, and microcline). Quartz, plagioclase, and orthoclase constitute about 95 percent by weight of the mineralogy with accessory minerals of glauconite, goethite, biotite, muscovite, magnetite, and minor amounts of ferroaluminosilicates and oxides (Barber and others, 1992). Clay minerals are sparse, with trace amounts (less than 5 percent by weight) of kaolinite, muscovite, chlorite, and some smectite. Magnetite is present in some areas, as are ferruginous, manganiferous, and organic coatings on gravels and sand grains.

Ground-Water Chemistry

Water chemistry and the distribution of solutes associated with the sewage plume are described by LeBlanc (1984) and Lee (1991). Background water chemistry is dilute and generally contains less than 150 mg/L dissolved solids (table 1). Hydrochemical facies range from no dominant cations or anions to sodium bicarbonate- or sodium chloride-dominated water. Waters that contain large concentrations of dissolved solids (greater than 100 mg/L) and are dominated by sodium and chloride ions indicate possible contamination from winter road-salting practices (D.R. LeBlanc, U.S. Geological Survey, oral commun., 1988). Ground water containing sewage effluent has substantial amounts of dissolved boron (up to 400 µg/L); whereas background water generally contains less than 50 µg/L dissolved boron (LeBlanc, 1984). All ground-water samples used in this study contain less than 50 µg/L dissolved boron and are considered uncontaminated by the sewage effluent. Samples from sites F294, F357, F358, F373, and F433 in map view appear to be from the contaminant plume, but, in reality, are from uncontaminated water above the sewage plume (fig. 1). The plume is overlain by up to 45 ft of uncontaminated ground water derived from precipitation that recharges the aquifer. Incongruent dissolution of feldspars to kaolinite has been shown to be a reaction consistent with observed water chemistry (Lee, 1991).

\[
\text{(albite)} + 2\text{Na}^+ + 2\text{HCO}_3^- + 4\text{H}_4\text{SiO}_4 \\
\text{(kaolinite)}
\]

(1)

If a homogeneous mineral assemblage and uniform recharge chemistry are assumed, then the chemical samples collected at increasing depths in the aquifer at all sites would be expected to show an increase in the chemical evolution of water resulting from increased contact time with the aquifer matrix. At some of the well sites, however, concentration of dissolved solids, which can indicate the degree of chemical evolution, decreases with depth (Lee, 1991).

Reaction Model

Based on observed chemical data, aquifer mineralogy, and chemical composition of recharge, it is possible to construct a reaction sequence for the chemical evolution of background water in the glacial sand and gravel aquifer. The extent of chemical reaction of silicate hydrolysis is determined from the acid content of the recharge water, which is a function of the amount of CO\(_2\) entering the ground-water system (Busenberg and Clemency, 1976).

Variations in chemical data are probably attributable to nonuniform distributions of CO\(_2\) in recharge water over the project area. This condition can occur because of areas of thin soil cover over the quartz sands and the effects of local differences in land cover, such as bare or poorly vegetated areas, mixed hardwood and conifer woodlands, large grassy areas on Otis Air Base and local parks, and cultivated grassy areas in suburban landscaping and golf courses. Variations in land cover have been shown to affect water chemistry in the unsaturated zone (Moss, 1990). These surficial features in the study area could affect CO\(_2\) production in the unsaturated zone.
Figure 1. Water-table map and locations of background water samples for the area of investigation.
ro
_t

o

1
2
3
4
5
6
1
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36

Mean

S3 13.038
S3 13.060
S3 13.080
S315.149
S31 6.082
S316.134
F234.099
F235.094
F238.106
F240.095
F24 2.077
F290.09 1
F294.064
F294.109
F299.020
F357.079
F357.099
F358.049
F358.089
F373.060
F373.ll 3
F4 12.042
F4 12.064
F4 12.078
F4 12.091
F41 2.108
F418.089
F418.103
F41 8.122
F418.141
F433.064
F433.090
F433.104
F436.036
F436.060
F436.076

38
60
80
149
82
134
99
94
106
95
77
91
64
109
20
79
99
49
89
60
113
42
64
78
91
108
89
103
122
141
64
90
104
36
60
76

Depth
below
land
surface
Well no. Site no. (feet)
9.0
10.0
10.0
13.0
11.0
11.0
10.0
10.5
10.0
9.5
10.0
10.0
10.0
9.5
9.0
9.5
12.2
10.5
9.5
13.0
12.2
10.0
9.5
9.5
9.5
9.5
9.5
9.5
9.5
9.5
9.0
9.0
9.5
10.0
13.0
9.0

Temperature
<°C)
5.70
5.60
5.90
6.08
6.50
6.50
5.70
5.60
5.70
5.80
5.80
6.20
5.80
6.30
5.40
5.60
5.60
5.50
6.00
5.68
6.31
5.50
5.80
5.50
5.50
5.70
5.80
6.20
6.40
6.40
5.50
5.90
6.30
5.60
5.76
6.70
68

37
65
47
61
139
64
64
66
70
36
38
61
56
75
59
63
45
25
33
53
100
28
81
170
182
120
54
72
65
63
44
71
78
31
54
81

PH
(units)

5.88

Calculated
dissolved
solids

4.22

0.93
2.40
2.60
2.17
27.00
3.90
3.90
4.20
4.50
1.50
1.50
4.40
1.40
8.80
7.70
1.80
1.79
1.10
1.20
1.75
8.82
0.66
0.54
3.30
4.40
3.20
3.70
6.70
5.10
4.40
1.40
2.60
5.50
0.88
2.70
12.00

Ca

2.52

0.89
3.00
2.30
1.10
7.10
2.80
2.80
1.90
4.10
1.80
1.90
2.00
1.80
4.30
1.80
3.20
2.06
0.85
0.96
1.66
3.36
1.20
1.00
4.50
5.90
3.50
3.20
3.00
2.30
2.10
1.80
2.40
2.40
1.20
1.81
2.90

Mg

12.93

9.30
12.00
6.30
7.94
14.00
6.70
9.60
7.20
8.20
5.80
6.30
8.50
15.00
14.00
5.40
13.00
6.85
4.00
5.70
10.50
15.30
4.40
25.00
52.00
54.00
34.00
7.20
10.00
9.70
9.30
8.80
17.00
16.00
5.80
10.70
10.00

Na

1.23

0.80
1.60
0.80
0.52
5.30
4.40
1.40
1.60
0.90
0.50
0.60
0.80
0.70
1.10
1.10
0.90
0.60
0.90
0.50
0.68
1.42
0.50
0.90
1.70
2.10
0.90
0.80
1.00
1.20
1.00
0.90
1.30
1.50
1.00
0.71
1.70

K

6.92

3.48
3.01
3.18
11.98
35.78
10.02
5.73
3.29
4.08
4.62
6.68
10.48
2.05
24.01
2.79
4.04
9.99
0.75
3.57
5.99
40.65
0.87
2.00
0.50
2.06
3.88
2.34
7.98
14.37
13.65
2.19
8.53
18.11
1.74
6.99
33.67

HCO3

9.8

5.7
21.0
15.0
7.7
22.0
16.0
17.0
25.0
27.0
5.4
7.3
6.8
4.8
4.9
9.1
13.0
5.3
4.3
5.8
6.5
6.0
6.0
19.0
5.3
7.4
7.1
4.6
5.9
7.2
6.1
7.0
9.0
10.0
6.0
4.5
13.0

S04

19.2

10.0
12.0
6.8
12.0
37.0
8.6
11.0
12.0
9.8
10.0
9.2
9.0
24.0
14.0
9.0
16.0
11.2
7.8
7.0
14.6
16.2
9.3
27.0
94.0
100.0
60.0
16.0
21.0
9.7
9.4
13.0
23.0
12.0
9.6
19.5
12.0

Cl

4.14

2.08
3.54
2.44
1.42
1.82
5.76
5.76
3.37
3.99
0.71
0.44
13.70
0.01
0.44
17.20
4.87
3.30
0.00
1.82
5.75
9.29
0.00
0.53
1.86
0.00
2.30
8.86
10.60
6.64
10.10
4.03
3.94
8.41
0.00
1.50
2.39

NO3

10.09

6.20
8.70
9.50
11.19
12.00
12.00
11.00
9.20
9.80
8.30
8.60
12.00
7.90
19.00
6.90
8.30
8.73
6.00
9.00
8.99
19.47
5.90
6.60
6.80
7.50
7.30
9.20
11.00
18.00
16.00
6.70
9.10
16.00
6.30
9.22
15.00

SiO2

7.4

11.2
10.6
11.4
11.0
0.8
1.8
10.3
9.0
9.4
10.8
10.7
1.4
10.8
2.0
9.5
10.2
9.7
12.2
5.4
8.2
0.1
11.2
11.1
9.0
6.4
6.0
4.8
5.7
2.0
3.9
9.7
9.6
0.5
8.8
11.0
0.2

0.506

0.378
0.396
0.236
0.629
1.086
0.306
0.618
0.428
0.438
0.418
0.599
0.476
0.183
0.950
0.567
0.537
1.270
0.122
0.228
0.640
1.530
0.143
0.179
0.079
0.329
0.418
0.210
0.364
0.502
0.477
0363
0.643
0.718
0.232
0.640
0.867

DisTotal
solved
CO2
C>2
(mmol/L)

Table 1 . Well numbers, depths, and water-chemical data for background water samples from the Cape Cod site (Chemical data are in milligrams
per liter unless otherwise specified)


and the subsequent flux of water and CO₂ through the unsaturated zone to the water table.

Significant vertical variations of chemical constituents can indicate one or more components of inhomogeneity of the chemical system. This inhomogeneity complicates development of a single quantitative mass-transfer model. The simulation process is further complicated by the difficult task of collecting chemical data along true flow paths in a water-table aquifer for comparison with results of geochemical mass-transfer models.

**CO₂ IN THE UNSATURATED ZONE**

In order to improve the understanding of CO₂ variability in recharge water in the project area, it was necessary to analyze for CO₂ concentrations in the unsaturated zone for the different land uses. Because much of the production of CO₂ occurs in the root zone of the soil and subsoil, the CO₂ concentration can vary significantly from season to season and with depth within the unsaturated zone (Reardon and others, 1979; Wood and Petraitis, 1984).

**Land Use**

Although the project area contains parks, residential areas, golf courses, a wildlife sanctuary, Otis Air Base, and other land uses, four principal types of land cover affect CO₂ production in the unsaturated zone. These are: areas where vegetative cover is sparse to absent, such as gravel pits and utility right-of-ways; mixed hardwood and conifer woodlands; grassy areas of parks, and much of Otis Air Base; and landscaped residences, and golf courses (fig 2).

**Methods**

Twenty sites in the project area were selected to sample and analyze soil gases (fig 2). Four were selected to show typical analytical results (fig. 3a-3d). Gas samples were withdrawn through a 1/2-inch-diameter hollow probe driven to a specified depth. Concentration profiles of CO₂ in unsaturated zone gas were obtained at each site to depths of up to 12 ft. Samples were collected over five consecutive seasons represented by the months of November 1991, February 1992, May 1992, July 1992, and November 1992. Samples were collected by first withdrawing the unsaturated-zone gases at a rate of 1 L/min with a peristaltic pump through intake slots near the base of the probe set to the specified depth. A constant value could usually be obtained by pumping for about 1 minute per ft of probe. Samples were withdrawn through the silicon tubing attached to the probe using a 50-mL plastic syringe with needle. The sample was immediately injected into a field gas chromatograph, which was equipped with a thermal conductivity detector. Peak separation of the CO₂ component of the gas was achieved using a micro-column packed with the HayesSep A and following the conditions of temperature and flow rate recommended in the user's manual for the equipment. The chromatograph contains an internal reservoir that accurately subsamples and passes the gas through the analytical column. Analytical precision was ± 1 percent and accuracy was ± 2 percent. Concentration of CO₂ was measured in parts per million, volume/volume. Calibration of the instrument was achieved using commercial standard gases.

**Results of Gas Sample Analyses**

Selected sites representative of results of the sampling for four significant land uses (Site a, grassy field; Site K, gravel pit; Site O, woodland; Site Q, golf course) are shown in figures 3a-d. Ranges of CO₂ concentrations given below represent approximate ranges of values in the subsurface from the actual data at each site. The smallest concentrations of CO₂ were in the gravel-pit areas where CO₂ ranged from about 500 to 2,000 ppm. Much of the vegetation had been removed at these locations, and the generation of CO₂ at the root zone was probably limited. The woodland areas contained the next smallest concentrations of CO₂—about 2,000 to 8,000 ppm. Woodlands were characterized by a moderate density of hardwood-conifer mix of trees, and low density ground cover with some decaying vegetation and mulch. CO₂ data from the woodlands overlapped CO₂ data for uncultivated grassy areas—about 6,000 to 8,000 ppm. Uncultivated grassy areas were covered with slow-growing grasses that were maintained by occasional mowing but were not watered or fertilized. The largest concentrations of CO₂ were found in the cultivated grassy areas on the golf courses—10,000 to 50,000 ppm. Hybrid grasses, high growth density, intense watering, and fertilization are conducive to elevated production of CO₂ in the root zone.
Figure 2. Land-use map in the vicinity of Otis Air Base, Cape Cod, Massachusetts, showing well cluster locations and unsaturated-zone-gas sampling locations.
Figure 3. Selected sites of the four principal land uses in the vicinity of Otis Air Base showing concentrations of carbon dioxide (CO\textsubscript{2}) in unsaturated-zone gases.
Changes in CO₂ concentrations in gases of the unsaturated zone also were variable with depth, depending on the season and the land use. Concentrations of CO₂ in the unsaturated zone were greater than concentrations of CO₂ in the atmosphere. At gravel-pit areas (fig. 3a), changes in CO₂ concentrations with depth below the root zone (0 to 2 ft) were small to zero with increasing depth. At woodland sites (fig. 3b), CO₂ concentrations increased with increasing depth during all the seasons sampled. At uncultivated grassy field sites (fig. 3c), CO₂ concentrations decreased slightly with increasing depth. The CO₂ concentrations were usually largest in the upper part of the unsaturated zone because of the production of CO₂ in large concentrations in the root zone beneath the grasses. At golf-course sites (cultivated grasses) (fig. 3d), the largest variations in CO₂ concentration were found. Concentrations of CO₂ were observed to increase with depth, not change with depth, or decrease with depth, depending on the season of the year. These effects are presumed to result from photosynthetic activity of the cultivated grasses and production of CO₂ in the shallow root zone. At site Q (fig. 3d), CO₂ concentration decreased with increasing depth, and relatively large CO₂ concentrations were measured during the February 1992 sampling. These results reflect late winter growth of the golf-course grasses. Another possibility is ice that formed in the low-lying area of the sample site may have inhibited escape of CO₂ to the atmosphere from the unsaturated zone.

Small or no increases in CO₂ concentration with increasing depth indicate an unsaturated zone at near steady-state with CO₂ production from the vegetative cover. An increase in CO₂ concentration with depth implies lower CO₂ production in the root zone at the time of sampling than at some recent (within hours) previous time. A decrease in CO₂ concentration with depth implies that CO₂ production in the root zone is greater at the time of sampling than at some recent previous time. The response time of gas concentrations in the unsaturated zone to large amounts of CO₂ production in the root zone likely depends on the distance from the source of CO₂, the rate of gaseous diffusion, and the rate of downward movement of moisture. Although no time of response to CO₂ production in the root zone was determined for the various sites, the probable amount of time would be on the order of hours to days; achievement of true steady-state CO₂ concentrations in the unsaturated zone would be unlikely.

Gradients in CO₂ concentration in the unsaturated zone also depended on the season. During active vegetative growth—for example, in July 1992—CO₂ production in the soil zone developed decreasing CO₂ concentrations from the root zone to the water table. During dormant periods, especially in February 1992, the gradient was reversed, indicating that larger amounts of CO₂ may be dissolved by unsaturated-zone water and carried to the water table during periods of vegetative growth and root respiration in summer than during dormant periods in winter. CO₂ may then be lost from the aqueous phase through the unsaturated zone to the atmosphere when the gradient in the unsaturated zone is reversed during dormant periods in winter. The net amount of CO₂ that enters recharge water is determined by the amount of CO₂ generated in the soil and root zone less the amount of CO₂ lost to the unsaturated zone and the atmosphere. Thus, CO₂ concentration in recharge water in the project area is variable, depending to a large extent on the vegetative cover in the recharge area.

Application of Henry's law to analytical data of unsaturated-zone gases for the purpose of calculating aqueous CO₂ in recharge at 10 °C (typical temperature of shallow ground water, LeBlanc, 1984), produces the following approximate ranges of concentrations of CO₂ dissolved in recharge water for each of the four land uses:

- Gravel pits: 0.035 - 0.150 mmol/L
- Woodlands: 0.150 - 0.350 mmol/L
- Grassy fields: 0.250 - 0.350 mmol/L
- Golf courses: 0.400 - 1.000 mmol/L

The initial reaction model developed by Lee (1991) assumed consistent recharge-water chemistry, aquifer mineralogy, and generation of CO₂ during percolation of recharge through the unsaturated zone. In order to improve the comparison between the background chemical data and model results for solutes, pH, and CO₂, it was necessary to vary amounts of CO₂ available for chemical reaction in the computer code PHREEQE (Parkhurst and others, 1980). The chemistry of recharge water, CO₂ from decay of organic matter in the aquifer, and mineral mass transfers were held constant for each of the six models (table 2). Only CO₂ in recharge water was changed in each of the models. CO₂ model input to recharge water ranged from 0.035 to 1.00 mmol/L in order to simulate the CO₂ in unsaturated zones for each of the four land uses described above. The model results are presented in table 2; the results cover most of the observed ranges of concentrations of solutes and show chemical evolution of pH and total CO₂.
Table 2. PHREEQE mass-transfer simulations [Concentrations in millimoles per liter unless otherwise specified]

<table>
<thead>
<tr>
<th>RECHARGE WATER</th>
<th>Woodlands</th>
<th></th>
<th>Gravel Pits</th>
<th>Grassy Fields</th>
<th>Golf Courses</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Model 1</td>
<td>Model 2</td>
<td>Model 3</td>
<td>Model 4</td>
<td>Model 5</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.035</td>
<td>0.150</td>
<td>0.250</td>
<td>0.350</td>
<td>0.400</td>
</tr>
<tr>
<td>pH (units)</td>
<td>5.48</td>
<td>5.15</td>
<td>5.04</td>
<td>4.97</td>
<td>4.94</td>
</tr>
<tr>
<td>Ca</td>
<td>0.036</td>
<td>0.036</td>
<td>0.036</td>
<td>0.036</td>
<td>0.036</td>
</tr>
<tr>
<td>Mg</td>
<td>0.036</td>
<td>0.036</td>
<td>0.036</td>
<td>0.036</td>
<td>0.036</td>
</tr>
<tr>
<td>Na</td>
<td>0.205</td>
<td>0.205</td>
<td>0.205</td>
<td>0.205</td>
<td>0.205</td>
</tr>
<tr>
<td>K</td>
<td>0.011</td>
<td>0.011</td>
<td>0.011</td>
<td>0.011</td>
<td>0.011</td>
</tr>
<tr>
<td>Cl</td>
<td>0.216</td>
<td>0.216</td>
<td>0.216</td>
<td>0.216</td>
<td>0.216</td>
</tr>
<tr>
<td>SO₄</td>
<td>0.072</td>
<td>0.072</td>
<td>0.072</td>
<td>0.072</td>
<td>0.072</td>
</tr>
<tr>
<td>NO₃</td>
<td>0.004</td>
<td>0.004</td>
<td>0.004</td>
<td>0.004</td>
<td>0.004</td>
</tr>
</tbody>
</table>

Add Minerals to above Solution in 15 Steps

<table>
<thead>
<tr>
<th>NaCl (halite)</th>
<th>NaAlSi₃O₈ (albite)</th>
<th>KAlSi₃O₈ (orthoclase)</th>
<th>CaAl₂Si₂O₈ (anorthite)</th>
<th>Mg₅Al₂Si₃O₁₀ (chlorite)</th>
<th>CO₂ (carbon dioxide)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.038</td>
<td>0.300</td>
<td>0.075</td>
<td>0.900</td>
<td>0.251</td>
<td></td>
</tr>
</tbody>
</table>

Subtract (precipitate) Mineral from Solution at Each Step

<table>
<thead>
<tr>
<th>Al₂Si₂O₅(OH)₄ (kaolinite)</th>
<th>total subtracted in step 15</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.251</td>
<td></td>
</tr>
</tbody>
</table>

FINAL RESULTS

| CO₂           | 0.935     | 1.050     | 1.150     | 1.250     | 1.300     | 1.900     |
| pH (units)    | 6.60      | 6.49      | 6.40      | 6.34      | 6.31      | 6.05      |
| Ca            | 0.086     | 0.086     | 0.086     | 0.086     | 0.086     | 0.086     |
| Mg            | 0.061     | 0.061     | 0.061     | 0.061     | 0.061     | 0.061     |
| Na            | 0.430     | 0.430     | 0.430     | 0.430     | 0.430     | 0.430     |
| K             | 0.036     | 0.036     | 0.036     | 0.036     | 0.036     | 0.036     |
| Cl            | 0.241     | 0.241     | 0.241     | 0.241     | 0.241     | 0.241     |
| SO₄           | 0.072     | .072      | 0.072     | 0.072     | 0.072     | 0.072     |
| NO₃           | 0.004     | 0.004     | 0.004     | 0.004     | 0.004     | 0.004     |
| SiO₂          | 0.455     | 0.455     | 0.455     | 0.455     | 0.455     | 0.455     |
Figure 4 graphically depicts the chemical evolution of shallow ground water from the approximate ranges of CO₂ in recharge water for the four major land uses, as well as the actual chemical data for the 36 wells in the project area. With minor exceptions, the chemical data for wells generally are within the range of values prescribed by the models, indicating the principal conceptual reaction process of CO₂-controlled feldspar hydrolysis to kaolinite. Also, it is possible to estimate from the graph which type of land use and mechanism for CO₂ generation was prominent in the recharge area for each well sampled.

Figure 2 shows the principal land uses in the area of Otis Air Base, site locations of wells sampled, and site locations of samples of unsaturated zone gas samples. The land use in the vicinity of a particular water well likely will affect CO₂ concentration in the shallow ground water as a result of recharge through that land use. Different land uses upgradient may produce significantly different CO₂ concentrations in recharge, that may, in turn, affect chemical reactions along deeper flow paths in the downgradient direction. The result of this process would be small vertical gradients of concentrations of dissolved solids in ground water, increasing in some places and decreasing in others. For example, water from wells at site S313 show a slight increase in concentrations of dissolved solids from 38 ft to 60 ft below land surface. A decrease in concentration of dissolved solids was noted from 60 ft to 80 ft below land surface, however (table 1). This indicates an upgradient source of recharge to the deepest well (80 ft) through a land use that produces concentrations of CO₂ lower than recharge to shallower wells. Poorly vegetated areas or woodlands in the vicinity of S313 could be in the recharge area for well 3 (fig. 4). Recharge to wells 1 and 2 probably passed through greater CO₂-producing land uses such as grassy areas (fig. 4) on the sewage treatment facility.

CONCLUSIONS

Background ground water at the Otis Air Base site, Cape Cod, Massachusetts, contains small concentrations of dissolved solids (less than 150 mg/L). Solutes found having elevated concentrations in the study area are sodium, bicarbonate, and chloride. Sodium and chloride increases have likely resulted from the application of road salt for deicing roadways. The chemistry of ground water appears to be dominated by CO₂-controlled weathering of silicates, principally sodium feldspar, with the formation of kaolinite. Increases in depth in the aquifer do not always correlate with increases in concentrations of dissolved solids as might be expected for a relatively homogeneous chemical system. PHREEQE mass transfer modeling, based principally on incongruent feldspar dissolution,
has demonstrated that variable CO₂ uptake by recharge water in the unsaturated zone is one process that could account for some of the chemical differences observed in background water in the glacial outwash aquifer. Land use, such as bare or poorly vegetated areas, mixed hardwood and conifer woodlands, and grassy areas on Otis Air Base, in local parks, in suburban landscaping, and on golf courses, affect the production of CO₂ and its flux from the unsaturated zone into the aquifer. Measured amounts of CO₂ in gases of the unsaturated zone underlying the principal land uses and vegetative covers indicate large variations in the amount of CO₂ available to recharge waters. The amount of unsaturated-zone CO₂ that dissolves in recharge water ranges from about 0.035 to 1.00 mmol/L in the study area. The amount of CO₂ available to react with feldspar minerals in the aquifer determines, in part, the concentrations of dissolved constituents in the ground water. This relation can account for areas where concentrations of dissolved solids in ground water decrease with increasing depth when sodium and chloride ions from road salting are not involved.

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Heavy-Metal Transport in a Sand and Gravel Aquifer with Variable Chemical Conditions, Cape Cod, Massachusetts

By James A. Davis¹, Douglas B. Kent¹, Jennifer A. Coston¹, and Kathryn M. Hess²

Abstract

An overview is presented of a field-based research program that is examining the significance of chemical speciation and variable aquifer chemistry on the transport of toxic metals in ground water. Natural-gradient tracer tests and laboratory experiments with subsurface materials have been used to identify the most important chemical reactions that influence the transport of chromium(VI) and metal-ethylenediaminetetraacetic acid (EDTA) complexes in the aquifer at the Cape Cod Toxic-Substances Hydrology Research site. The field experiments are being conducted in an uncontaminated, recharge zone and a mildly reducing, sewage-contaminated zone of the shallow, sand and gravel aquifer. The results of several years of research at the site have been used to design a large-scale tracer test at the site (begun in April 1993) involving eight tracers (bromide, chromium, zinc, copper, lead, nickel, EDTA, and potassium). The new experiment will be the most complex and detailed investigation of multispecies, multireaction transport ever conducted in the field. The pertinent results of previous small-scale tracer tests are reviewed, and the objectives and expected results of the new tracer test are discussed.

INTRODUCTION

Chemical reactions can have a major effect on the transport of inorganic solutes (Yeh and Tripathi, 1991; Liu and Narasimhan, 1989). The reactivity of these solutes depends strongly on chemical speciation. Species that precipitate or are extensively adsorbed are highly retarded, whereas species that are soluble and weakly adsorbed can be mobile in ground water (Davis and others, 1991a). For example, zinc (Zn) has been shown to be extensively retarded in ground water when present as a free (uncomplexed) cation (von Gunten and others, 1991; Rea and others, 1991). In contrast, the formation of weakly adsorbing, anionic complexes greatly increases the mobility of Zn (Kent and others, 1991, 1992). Other metals, including Cu(II) (copper, in the plus two oxidation state) and a variety of radionuclides, have been shown to be mobile in ground water as a result of their presence as weakly adsorbing organic complexes (Jacobs and others, 1988; von Gunten and others, 1991; Killey and others, 1984). Changes in pH along ground-water flow paths can cause shifts in metal speciation from soluble to sparingly soluble species. In addition to complexation and acid-base reactions, oxidation-reduction (redox) reactions may cause changes in speciation that have a marked effect on transport. For example, aqueous Cr(VI) species (chromium, in the plus six oxidation state) are generally soluble and relatively weakly adsorbing; hence, they can be mobile in ground water. However, Cr(III) species, if uncomplexed, should be highly retarded in ground water because they are extensively adsorbed or insoluble (Kent and others, 1994). Other inorganic contaminants subject to changes in speciation due to redox reactions include selenium (Se), sulfur, arsenic, uranium, nitrogen, Cu, iron (Fe), and manganese (Mn).

Although considerable advances are being made in the development of mathematical algorithms (Yeh and Tripathi, 1991; Rubin, 1990), many practical problems remain if reactive-transport models are to be applied to ground-water systems in predictive simulations. For example, redox reactions are generally included in models as half-reactions, so that one can either impose a constant activity of the aqueous electron, or, by including both oxidation and reduction reactions and considering the conservation of electrons, one can allow the model to compute the redox equilibrium state and the resultant electron activity. In applying a model to a ground-water system, however, neither of these approaches may be satisfactory. Particular solutes of interest may not equilibrate with an electron activity that is estimated from measuring the species of major redox couples. Calculations assuming a conservation of electrons would require that all electron transfer reactions are accounted for in the model; this may be difficult when immobile organic matter or another reductant associated with the porous medium is the electron donor. When neither of these approaches apply, an important component of reactive-transport modeling will be detailed site characterization and laboratory studies that allow an identification of the important chemical reactions that need to be considered. This is the approach we have emphasized in our research on the transport of reactive metals. Adsorption reactions also require special considerations. Some reactive-transport models have relied on empirical parameters, such as distribution coefficients or isotherms determined in laboratory studies, to describe retardation of solutes during transport. While this approach may be satisfactory under constant chemical conditions, the surface complexation modeling approach will provide better results under conditions of variable chemistry (Davis and Kent, 1990). Adsorption of inorganic solutes is affected by competitive adsorption processes, solute speciation changes, and other factors under conditions of variable chemical conditions. In the surface complexation approach, adsorption is considered as a set of one or more chemical reactions involving an aqueous species, a surface site of the porous medium, and protons. In principle, reactions are required for each adsorbing solute; however, laboratory experiments may be used to minimize the number of reactions needed for a transport modeling application.

The purpose of this paper is to provide an overview of the research on multispecies transport at the Cape Cod site, including a discussion of the objectives of a new large-scale field experiment that was begun in April 1993. The new experiment is designed to evaluate the effects of speciation and variable aquifer chemistry on metal transport in ground water to a greater degree of complexity than has been done previously. To set the context of the research, the paper includes a review of the findings of previous research at the site that were pertinent to the design of the new field experiment.

SITE DESCRIPTION

The U.S. Geological Survey (USGS) has been conducting research for several years at a site in Falmouth, Mass., on Cape Cod (fig. 1). The research site is in an area of sand and gravel outwash that has been contaminated by land disposal of treated sewage for more than 50 years. A contaminant plume more than 5 km long has formed as a result of the sewage disposal (LeBlanc, 1984; Barber and others, 1988; Hess and others, 1991). The sewage plume sinks as it travels southward with the ground water. Average ground-water velocities determined from measurements of hydraulic conductivity, porosity, and hydraulic gradient range from 0.25 to 0.5 m/d (Garabedian and others, 1991; LeBlanc and others, 1991).

In 1984-85, the USGS installed a spatially dense well field in an abandoned gravel pit at this site to begin three-dimensional studies of solute transport in a field setting. A large number (640) of multilevel sampling devices (MLS) were installed, arranged in 71 rows which extend about 300 m downgradient from the first row. In preparation for the project described here, an additional 100 MLS were installed in the field during 1992. Each multilevel sampling device includes 15 sampling ports spaced 25 to 76 cm apart vertically to provide vertical profiles of tracer concentrations. In total, there is an array of over 11,000 sampling points downgradient from the injection wells, allowing detailed and statistically significant studies of transport to be conducted.

The aquifer contains two zones with distinct chemical characteristics (Kent and others, 1994). The uncontaminated recharge zone has high concentrations of dissolved oxygen (DO), low pH (5.1), and low concentrations of dissolved salts (about
EXPLANATION

--- 13.45 --- WATER-TABLE CONTOUR, AUGUST 2, 1985 --
Shows altitude of water table. Contour interval
0.05 meters. Datum is sea level.

Figure 1. Location of large-scale natural-gradient tracer test. (Modified from LeBlanc and others, 1991, fig. 4.)
30 μS/cm). The sewage-contaminated zone is suboxic (mildly reducing) with a higher pH (6.1) and high concentrations of dissolved salts (about 300 μS/cm). Fe(II) and dissolved sulfide are both below detection limit in the region of the anoxic zone penetrated by the MLS's; dissolved Mn concentrations range from 5 to 10 μM.

BACKGROUND

Large-scale Tracer Test

The site was used during 1985-87 for a detailed natural-gradient study of bromide, lithium, and molybdate transport (LeBlanc and others, 1991; Garabedian and others, 1991). The tracer test was designed to examine the relationship between field-scale dispersion and aquifer heterogeneity developed by Gelhar and Axness (1983). Major conclusions of the study were as follows: (1) longitudinal mixing was the dominant dispersion process; (2) transverse horizontal and vertical dispersion were relatively small; and (3) horizontal displacement of the injected solute cloud was accurately predicted using estimates of the hydraulic conductivity, porosity, and measured hydraulic gradient (Garabedian and others, 1991). Solute concentrations were highly variable and difficult to predict on a small scale but the average characteristics (the spatial moments) could be predicted. Molybdate transport depended on many factors, including pH and the concentration of other anions (for example, phosphate and sulfate), and the sorption isotherm was nonlinear (Stollenwerk and Grove, 1987).

Small-scale, Multispecies Tracer Tests

The large-scale tracer test conducted in 1985-87 characterized the hydrology of the site in great detail. This comprehensive work and the dense array of MLS have made it possible to conduct more complex geochemical transport experiments with reactive tracers. The Solute Partitioning project (USGS, Menlo Park, Calif.) has been conducting field- and laboratory-scale experiments to study the transport of solutes for which speciation is important (Kent and others, 1994, 1995, 1991, 1992; Anderson and others, 1994; Davis and others, 1991b). Our objectives are to: (1) identify the important chemical processes affecting transport, (2) examine the relations among chemical and physical factors affecting transport, and (3) stimulate the development of coupled flow and geochemical models that describe the transport of these solutes.

Twelve small-scale natural-gradient tracer tests were performed during 1988-92 to study the transport of Zn, nickel (Ni), ethylenediaminetetraacetic acid (EDTA, a metal-complexing agent), Cr(VI), and Se(VI) in oxic and suboxic zones of the shallow sand and gravel aquifer at the Cape Cod site (Kent and others, 1992, 1994, 1995; Davis and others, 1991b). In each test, approximately 400 or 600 L of ground water were withdrawn from an MLS into an acid-washed polyethylene bag; the tracers were dissolved therein, and the "spiked" ground water was injected into several ports of the same or another MLS. Bromide ion (Br) was used as a conservative tracer. Breakthrough of the tracers was monitored at samplers downgradient from the injection MLS. Typically the movement of the tracers was monitored for several weeks following the injection; the travel distance for bromide ion was usually less than 20 meters during the experiments. Methods for the measurement of tracers are given in Kent and others (1994).

Cr transport showed a marked dependence on its speciation and the chemical composition of the aquifer. In the oxic zone, Cr(VI) transport was retarded relative to Br and there was little evidence for reduction (Kent and others, 1995). This was likely due to adsorption of Cr(VI) onto minerals such as Fe and Mn oxides, which is favored in the oxic zone by the low pH and low concentrations of anions that compete for adsorption sites, such as sulfate and phosphate. In the suboxic zone, Cr transport was increasingly attenuated with distance transported, but was only slightly retarded. The attenuation was due to reduction of Cr(VI) to Cr(III), which is immobile (Kent and others, 1994). Analysis of the speciation of dissolved Cr showed that Cr(VI) was the only mobile species. Cr(VI) transport was only slightly retarded in the suboxic zone because Cr(VI) adsorption was decreased by the higher pH and greater concentrations of competing sorptive anions present. The amount of Cr(VI) reduced along a flowpath appeared to be limited by the rate of diffusive transport to reductive sites present in the porous medium. Prediction of the amount of Cr reduced from thermodynamic considerations alone was not possible.
Transport of Zn- and Ni-EDTA complexes were also affected by the chemical characteristics of the site. In the oxic zone, both Zn and Ni transport were retarded. Dissolution of iron and aluminum oxides (enhanced by the low pH in this zone) resulted in dissociation of Zn from EDTA, with exchange for Fe and Al, which form very strong complexes with EDTA. From laboratory experiments, it is known that Zn$^{2+}$ adsorbs extensively on the aquifer sediments in the absence of EDTA (Davis and others, 1993), so the transport of Zn$^{2+}$ would be significantly retarded after dissociation from EDTA. In contrast, the rate of NiEDTA dissociation was slow. Even though the local conditions probably favored exchange of Fe for Ni in EDTA complexes at chemical equilibrium, this reaction did not occur to a significant extent.

At the suboxic site, Zn and Ni transport were only slightly retarded, and the breakthrough curve for total EDTA showed the same degree of retardation (Kent and others, 1992). Thus, both Zn and Ni were transported as EDTA complexes. In the transition zone between the oxic and suboxic zones, Zn concentrations increased downgradient from the injection MLS, as excess EDTA induced the desorption of Zn contamination that was adsorbed on the porous medium (Kent and others, 1991). The source of Zn contamination on the porous medium in the transition zone is the sewage effluent plume (Rea and others, 1991).

NEW LARGE-SCALE TEST WITH REACTIVE TRACERS

A new large-scale field experiment was begun on April 21, 1993, to study in detail the effects of chemical speciation on reactive transport. Approximately 10,000 L of native ground water were pumped into a clean plastic tank in which the chemical tracers were mixed with the water. The tracers added to the ground water were Br, potassium, Cr(VI), Zn, Ni, Cu, and lead (Pb), and EDTA. The spiked ground water was pumped into three ports each of six custom-designed MLS over an 8-hour period. All MLS surrounding and within the tracer cloud -- that is, spatial "snapshots" -- were sampled shortly after the injection and are now being sampled on a monthly basis until November 1993. The spatial sampling will then be performed on a bimonthly basis until July 1994. Approximately 40,000 water samples will be collected for analysis of tracer concentrations over the duration of the project. Water samples will be analyzed after each sampling trip to determine the concentrations of all chemical tracers as well as several other elements. Dissolved oxygen, pH, and other water quality characteristics will be determined in selected field measurements at the time of water sampling.

The tracer test will exploit the vertical gradient in ground-water chemistry at the site to study transport under variable chemical conditions. Small-scale tracer tests conducted previously at the site have shown that metal transport is controlled by a different set of chemical reactions in the oxic and suboxic zones. Therefore, to show the importance of speciation and chemical conditions on metal transport, tracers were injected in the new test over a larger vertical interval that includes both zones. This vertical interval also has a significant pH gradient that will affect the adsorption of metal ions. The top of the tracer cloud will move within the oxic zone, and the lower part of the tracer cloud will move within the suboxic zone. In the transition zone, at the interface between these two zones, is the well-defined region of zinc contamination derived from sewage effluent. In this zone, the Zn contamination will affect metal transport via competitive processes (for both adsorption and aqueous complexation).

The data collected will allow detailed characterization of the metal transport behavior, and the effects of chemical processes on metal transport will be quantified. Chromium(VI) transport is expected to be controlled by sorption reactions in the upper part of the tracer cloud and redox reactions in the lower part of the tracer cloud. Lead, copper, zinc, and nickel mobility in the aquifer will be controlled by several chemical factors, including the concentration of EDTA, concentrations of other cations competing for coordination with the ligand, and the abundances of adsorbing mineral phases in the aquifer. Because of differences in the thermodynamics and rates of dissociation of metal-EDTA complexes, it is expected that Pb transport will be attenuated first in the suboxic zone, followed by Zn and then Cu. Ni probably will not be dissociated from EDTA in the suboxic zone during the test, and its transport will be controlled by adsorption of the Ni-EDTA complex only. In the zone of zinc contamination, zinc will be desorbed by complexation with any excess EDTA and readorsed farther downgradient as dispersion lowers the concentration of the ligand.
The research will allow observations of metal transport over a significant distance (up to 200 m) and time (up to 1.5 years), depending on the degree of attenuation and retardation during transport. The data collected will then allow a comparison of chemical reaction parameters (for example, sorption coefficients and redox reaction rates) in solute-transport models with those that have been measured in laboratory experiments and small-scale tracer tests at the site. The rate of Cr(VI) reduction observed in laboratory experiments suggests that slow processes may be more important in a large-scale tracer test. A large-scale tracer test also will allow an examination of the effect of dispersion on chemical speciation and transport. The physical heterogeneity of the aquifer has made it difficult to model transport in small-scale experiments. The greater transport distance and larger dimensions of the tracer cloud envisioned for the large-scale tracer test will improve the quality of mass balances for tracers and make it possible to consider certain simplifying assumptions within a solute-transport model. In addition to these objectives, the research will identify general methods and approaches for successful prediction of metal transport and stimulate the development of transport models that account for the effects of variable chemistry on solute mobility.

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Evaluation of Geochemical Indicators of Metal Adsorption in a Sand and Gravel Aquifer, Cape Cod, Massachusetts

By Christopher C. Fuller1, Jennifer A. Coston1, James A. Davis1, and Eleanor Dixon1

Abstract

The geochemical properties of an aquifer sand that control metal-ion adsorption were investigated to determine their potential use as indicators of the spatial variability of metal adsorption in the aquifer. Over the length of a 4.5-meter long core, lead (Pb) and zinc (Zn) adsorption varied by a factor of two and four, respectively. Pb2+ and Zn2+ are adsorbed primarily by iron and aluminum oxide coatings on quartz-grain surfaces. Upon normalization to surface area, both Pb2+ and Zn2+ adsorption were significantly correlated with the amount of iron and aluminum dissolved from the aquifer material by partial chemical extraction. The use of partial chemical extraction combined with surface-area measurement as a potential indicator of metal adsorption in other aquifers needs to be tested.

INTRODUCTION

Modeling the transport of metals requires use of accurate adsorption coefficients to describe metal ion sorption onto surfaces of aquifer solids. In natural systems, metal adsorption is commonly thought to be controlled by iron (Fe) and aluminum (Al) oxide coatings on particle surfaces (Davis and Kent, 1990). Metal adsorption by pure oxide phases is well described by surface-complexation models (Dzombak and Morel, 1990). However, determining the appropriate type and surface density of adsorption sites can cause difficulties in applying surface-complexation models to mixed assemblages of mineral surfaces comprising natural systems (Davis and Kent, 1990). In addition, the spatial variability in adsorption properties within an aquifer, like hydraulic conductivity (Hess and others, 1992), can be of importance in describing solute transport and need to be accounted for (Robin and others, 1991).

A study of the spatial heterogeneity of metal-ion adsorption and hydraulic conductivity at a site on Cape Cod has recently been completed (Davis and others, 1993). The objectives of the study were to determine the predominant metal adsorbing surface in the aquifer solids, to quantify the spatial variability of metal adsorption and hydraulic conductivity, and to determine if a geochemical property of the aquifer material can be used as an indicator of the surfaces controlling lead (Pb2+) and zinc (Zn2+) adsorption. An analysis of the spatial variability of metal adsorption and hydraulic conductivity is included in this volume (Hess and others, 1995).

This paper summarizes the results of the evaluation of geochemical indicators of metal adsorption in the aquifer and their potential use for describing the spatial variability of lead and zinc adsorption in the aquifer sand. For example, if the variability in metal ion adsorption is caused by a greater reactivity with the surfaces of a secondary mineral phase or coating, the partial chemical extraction results could describe the variability of the reactive phase. The properties of the aquifer sand evaluated include Pb2+ and Zn2+ adsorption, surface area, grain-size distribution, and partial chemical extraction.

Aquifer material was collected at the U.S. Geological Survey Toxic Substances-Hydrology Research site near Falmouth, Massachusetts (fig. 1). The site is a shallow, unconfined aquifer of glacial outwash (LeBlanc and others, 1991). Sediments in the aquifer consist predominantly of medium to coarse sand, with localized zones of gravel, fine sand, and silt. The aquifer has an average porosity of 0.39 and an average ground-
MINERAL SURFACES THAT CONTROL METAL ADSORPTION

Adsorption of Pb$^{2+}$ and Zn$^{2+}$ by the aquifer sand is less dependent on pH than is typically observed for pure oxides (Coston and others, 1992). The adsorption edges span 2 pH units compared to 1 unit for pure oxides (Davis and Kent, 1990). Adsorption of Pb$^{2+}$ and Zn$^{2+}$ on the highly weathered, coarse aquifer sand was dominated by quartz grains (95 percent by weight) in the sand (<1,000 µm diameter). The reactivity of the natural quartz surfaces was attributed to 10- to 300-nm thick coatings on the sand grains that are composed of surface precipitates of complex mixed oxides and silicates containing high concentrations of Fe and Al. The coatings are derived from the weathering of feldspars and other accessory minerals in the aquifer. A decrease in Pb$^{2+}$ adsorption was observed with a diamagnetic sand treated with hydroxylamine hydrochloride to remove Fe- and Al-oxide coatings. These results indicate that partial chemical extractions could be useful as indicators of metal adsorption.

METHODS

Collection of Aquifer Material

Cores for the spatial heterogeneity study (Fuller and others, 1991) were collected using a wireline-piston core barrel and plastic core liners (Zapico and others, 1987) and were frozen until used. Three consecutive 1.5-m long cores were collected from each bore hole. The material from one transect core, F415 C38 (fig. 2), was used for this study. Cores were subdivided into 10-cm-long vertical subsamples, dried in a laminar flow hood, and sieved to remove grains greater than 1,000-µm diameter.

Determination of Variability of Metal Adsorption by Batch Experiments

For each vertical subsample, Pb$^{2+}$ and Zn$^{2+}$ adsorption were measured in three batch experiments using a sand to artificial ground water (AGW) ratio of 50 g/L. Pb$^{2+}$ and Zn$^{2+}$ were added simultaneously from a combined stock solution to yield total concentrations of 20 and 5 µM, respectively. Each of the three batch experiments for a subsample was designed to attain a different pH value after 48 hours of reaction (pH 5.1, 5.3, and 5.5), by addition of predetermined aliquots of 0.04M NaOH or 0.04M HNO$_3$. The 48-hour reaction period was chosen on the basis of adsorption kinetic experiments (Davis and others, 1993). The amount of metal adsorption was calculated from the change in the dissolved metal concentration. Metal concentrations were determined by inductively coupled plasma atomic emission spectrometry (ICAP-AES). Adsorption results for each of the pH values for each vertical subsample were normalized to pH 5.3 using the Kurbatov equation with a macroscopic proton coefficient of one (Kurbatov and others, 1951; Honeyman and Leckie, 1986), and averaged.

Characterization of Aquifer Material for Indicators of Metal Adsorption

Three partial-chemical-extraction methods were used to determine if Pb$^{2+}$ and Zn$^{2+}$ adsorption correlate with the amount of Fe, Al, and manganese (Mn) extracted from the aquifer material. Partial chemical extractions of aquatic sediments and aquifer materials are commonly used to estimate the partitioning of trace metals among secondary phases such as amorphous Fe, Al, and Mn oxides (Tessier and others, 1979; Chao, 1984; Robinson, 1984/85; Tessier and others, 1989).

Sand samples were treated with hydroxylamine hydrochloride (0.25 M NH$_2$OH•HCl in 0.25 M HCl) at 50 °C for 0.5 and 72 hours. Hydroxylamine-HCl (HA) extracts iron by reductive dissolution at low pH (Chao and Zhou, 1983). The HA extraction is not selective for Fe; for example, Al and Mn also were extracted from the sand. Al dissolved by HA could be caused by partial dissolution of feldspars and other aluminosilicate phases as well as aluminum oxide coatings on grain surfaces. The HA extraction for 0.5 hours was chosen because it has been reported to be the most effective method for selective dissolution of amorphous Fe oxyhydroxides with minimal dissolution of crystalline Fe oxyhydroxides (Chao and Zhou, 1983). Dissolved Fe concentrations increased over time in HA extracts of a 250 to 500-µm diamagnetic fraction of the sand, reaching a constant concentration after 48 hours of extraction. However, dissolved Fe increased through 96 hours of extraction of
Figure 2. Lead and zinc adsorption in micromoles per gram of sand and percentage of total metal as a function of core interval altitude (meters above sea level) in core F415 C38. Horizontal error bars represent one standard deviation of the three averaged adsorption values. Vertical error bars represent the depth range of core intervals.

The total adsorption site density of mineral surfaces can be estimated from the surface area determined by gas adsorption (Davis and Kent, 1990). Single-point surface areas were measured by nitrogen gas adsorption on samples from core F415 C38. Grain-size distributions were determined on the less than 1,000-μm split of each vertical subsample by dry sieve analysis (American Society for Testing Materials, 1986).

RESULTS AND DISCUSSION

The variability of Pb$^{2+}$ and Zn$^{2+}$ adsorption in core F415-C38 (fig. 2) was typical of others in the transect (Davis and others, 1993). Pb$^{2+}$ adsorption varied by about a factor of two over the length of the core. Zn$^{2+}$ adsorption was less than that observed for Pb$^{2+}$, but varied by about a factor of three or four.

The surface area of subsamples from core 38 varied by a factor of two, with no apparent trend with
Table 1. Range in concentrations of iron, aluminum and manganese in core F415 C38 from 0.5- and 72-hour hydroxylamine and 24-hour dithionite-ammonium citrate extractions.

[[mol/g, micromoles per gram; [mol/m², micromoles per square meter; HA, hydroxylamine hydrochloride; DC, dithionite-ammonium citrate; Max, maximum concentration; Min, minimum concentration; Al, aluminum; Fe, iron; Mn, manganese]]

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depth. The tenth-percentile grain-size diameter, d_{10}, ranged from 0.174 to 0.362 mm in this core; d_{10} did not appear to change as a function of depth. Generally, the surface area decreased as d_{10} increased but did not appear to vary linearly with d_{10}. Instead, the relation between surface area and d_{10} might be better described by a parabolic function (Davis and others, 1993).

The range in concentrations of extracted Fe, Al and Mn in this core is shown in table 1. No apparent trend with depth was observed for any of the extracted metals. In units of micromoles per g, Al was significantly correlated with Fe in the three extractions, despite the greater selectivity of DC for Fe over Al. A linear correlation between two variables is considered significant if the correlation coefficient (r) is greater than the critical value of r for the 5 percent level of significance (Sokal and Rohlf, 1973). The strong correlation of Fe and Al in all three extractions indicates that the source of both metals is largely the dissolution of mixed-oxide coatings on the grain surfaces. If the source was from dissolution of separate minerals instead, such as a mixture of magnetite and feldspar, it seems unlikely that the abundances of these minerals would covary throughout the core. Extracted Mn was strongly correlated with Fe in both the 0.5- and 72-hour HA extractions, but not in the DC extraction. Extracted Fe, Al, or Mn by the three methods did not correlate with surface area. The lack of correlation is probably due to the fact that the surface area is indicative of the entire surface area of the samples, including surfaces other than those containing the extracted elements.

Potential Use of Geochemical Properties as Indicators of Metal Adsorption

Linear regressions of the Pb^{2+} adsorption data in units of micromoles per gram of sand did not yield significant correlations with d_{10} (in mm) or surface area (in m²/g). This result indicates that Pb^{2+} adsorption occurs at specific areas on the sand surface that are more reactive, whereas the surface area is a measurement of the entire surface area. Pb^{2+} adsorption also was not correlated with 0.5-hour HA-extractable Fe, Al, or the sum of Fe and Al in units of micromoles per gram. The 0.5-hour HA extraction should dissolve amorphous coatings of Fe and Al oxides that are more reactive with respect to adsorption than crystalline oxides (Davis and Kent, 1990). However, significant correlations were observed for linear regressions of Pb^{2+} adsorption with 72-hour HA Al, and the sum of Fe and Al and with the DC Fe, Al, and the sum of Fe and Al (table 2). Because the molar ratio of Pb^{2+} adsorbed to Mn extracted was greater than 1 for all extractions, Mn was not used as a variable for correlation analysis with Pb^{2+}. No significant correlations were found between Zn^{2+} adsorption (in units of micromoles per gram) and surface area, grain size, or any elements determined in the three extraction methods.

Because the batch adsorption experiments were conducted using conditions of equal sand mass per volume of AGW, the adsorption and extraction data were normalized per unit surface area (micromoles per square meter) to eliminate this factor as a variable. Significant positive correlations between Pb^{2+} and Zn^{2+} adsorption and 0.5 hour HA, 72-hour HA, and DC extracted Fe, Al, and the sum of Fe and Al were obtained upon normalizing to surface area (fig. 3). Pb^{2+} (table 2) and Zn^{2+} adsorption were more highly correlated with the 72-hour HA- and DC-extracted Fe and Al than with the 0.5-hour HA extraction. Because Fe and Al are highly correlated with each other in all extractions, Pb^{2+} or Zn^{2+} adsorption each correlate well with extractable Fe, Al, and the sum of Fe and Al, when normalized to surface area. Therefore, the extraction data do not allow differentiation between metal adsorption onto Al or Fe phases.
Table 2. Summary of regression analysis for lead adsorption at pH 5.3 for subsurface samples of core F415 C38
[μmol/g, micromoles per gram; μmol/m², micromoles per meter squared; n-2, degrees of freedom; r, linear correlation coefficient; Pb, lead; Fe, iron; Al, aluminum]

<table>
<thead>
<tr>
<th>Dependent variable</th>
<th>Independent variable</th>
<th>n-2</th>
<th>r</th>
<th>r_{c}^{d}</th>
<th>slope</th>
<th>Intercept</th>
</tr>
</thead>
<tbody>
<tr>
<td>μmol/g Pb, Fe, Al</td>
<td>Pb 72 hr Al&lt;sup&gt;a&lt;/sup&gt;</td>
<td>19</td>
<td>0.60</td>
<td>.55</td>
<td>.006</td>
<td>.144</td>
</tr>
<tr>
<td></td>
<td>Pb 72 hr Fe+Al&lt;sup&gt;b&lt;/sup&gt;</td>
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<td>.55</td>
<td>.012</td>
<td>.121</td>
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<tr>
<td></td>
<td>Pb DC Al&lt;sup&gt;b&lt;/sup&gt;</td>
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<td>.62</td>
<td>.53</td>
<td>.082</td>
<td>.112</td>
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<tr>
<td></td>
<td>Pb DC Fe+Al&lt;sup&gt;b&lt;/sup&gt;</td>
<td>21</td>
<td>.64</td>
<td>.53</td>
<td>.011</td>
<td>.115</td>
</tr>
<tr>
<td>μmol/m² Pb, Fe, Al</td>
<td>Pb 0.5-hr Fe&lt;sup&gt;c&lt;/sup&gt;</td>
<td>24</td>
<td>.60</td>
<td>.50</td>
<td>.045</td>
<td>.718</td>
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<tr>
<td></td>
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<td>.50</td>
<td>.060</td>
<td>.533</td>
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<td>.030</td>
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<td>.365</td>
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<tr>
<td></td>
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<td>.88</td>
<td>.55</td>
<td>.010</td>
<td>.336</td>
</tr>
<tr>
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<td>.89</td>
<td>.55</td>
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<td></td>
<td>Pb DC Fe&lt;sup&gt;h&lt;/sup&gt;</td>
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<td>21</td>
<td>.87</td>
<td>.53</td>
<td>.111</td>
<td>.279</td>
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<tr>
<td></td>
<td>Pb DC Fe+Al&lt;sup&gt;b&lt;/sup&gt;</td>
<td>21</td>
<td>.82</td>
<td>.53</td>
<td>.015</td>
<td>.293</td>
</tr>
</tbody>
</table>

<sup>a</sup>72-hour hydroxylamine hydrochloride extraction at 50 °C.
<sup>b</sup>24-hour dithionite-ammonium citrate extraction.
<sup>c</sup>0.5-hour hydroxylamine hydrochloride extraction at 50 °C.
<sup>d</sup>Critical value of r for 1 percent level of significance.

![Figure 3. Lead adsorption (micromoles per meter squared) as function of 72-hour hydroxylamine hydrochloride extracted iron (micromoles per meter squared) for core F415 C38. Error bars present one standard deviation of averaged adsorption value and uncertainty in surface area and iron determinations.](image-url)
SUMMARY

The significant correlations between metal adsorption and the extracted Fe and Al (DC or 72-hour HA) suggest that extractable metals, combined with surface area measurements, could be used as an effective geochemical "indicator" of the potential variability of metal adsorption in this aquifer. Because of the many potential artifacts and time-intensive nature of adsorption experiments conducted with natural materials, simple laboratory characterization methods are needed to provide a first approximation of the adsorptive reactivity of site-specific materials at contaminated field sites. Although these measurements are not more accurate than carefully controlled adsorption measurements, the measurement of simple geochemical indicators could be preferable in site-assessment or other nonresearch-related applications. However, the usefulness of the indicator discovered in this study needs to be tested at several other sites before it can be considered an effective characterization tool.

REFERENCES


Spatial Variability of Metal-Ion Adsorption and Hydraulic Conductivity in a Sand and Gravel Aquifer, Cape Cod, Massachusetts

By Kathryn M. Hess1, James A. Davis2, Christopher C. Fuller2, and Jennifer A. Coston2

Abstract

The spatial variability of metal-ion adsorption and hydraulic conductivity was assessed from the results of laboratory experiments on 375 sediment samples collected from 14 boreholes in a glacial outwash, sand and gravel aquifer on Cape Cod, Massachusetts. Zinc and lead adsorption were measured in batch experiments. Hydraulic conductivity was estimated on the basis of grain-size distributions. Mean lead adsorption is greater than mean zinc adsorption; mean hydraulic conductivity is similar to that measured previously in this aquifer. All three properties vary significantly within the aquifer; variability in zinc adsorption is greater than variability in lead adsorption. A strong positive correlation is observed between the two metal-ion adsorptions. There is a statistically significant, but small, negative correlation between lead adsorption and hydraulic conductivity and a statistically insignificant negative correlation between zinc adsorption and hydraulic conductivity. Vertical correlation scales obtained by fitting an exponential model to experimental semivariograms equaled 0.10-0.26 meters for the hydraulic-conductivity and adsorption data sets. Similar vertical correlation scales were determined in an earlier study of the variability of hydraulic conductivity measured by use of permeameter and flowmeter tests. A horizontal correlation scale could not be identified in this study, possibly because the horizontal spacing between boreholes was large relative to the correlation scale, and the number of samples was small.

INTRODUCTION

The dispersion of reactive solutes, such as zinc and lead, during transport in the subsurface is greater than the dispersion of nonreactive solutes. Heterogeneity in the physical and geochemical properties of aquifer sediments and correlations among these properties are thought to control field-scale dispersion of reactive species (Garabedian and others, 1988; Kabala and Sposito, 1991; Miralles-Wilhelm, 1993). A negative correlation between hydraulic conductivity (K) and adsorption has generally been assumed; surface area and, therefore, adsorption tend to increase as grain size and, therefore, K decrease. Several detailed investigations of the spatial structure of the hydraulic-conductivity distribution in aquifers have been reported (Sudicky, 1986; Hess and others, 1992; Rehfeldt and others, 1992). To date, however, few attempts have been made to quantify spatial variability in adsorption and correlation among physical and geochemical properties that affect adsorption; Robin and others (1991) found a statistically significant negative correlation between hydraulic conductivity and distribution coefficient for 1,279 core samples from the Base Borden aquifer in Ontario, Canada. The ultimate objectives of our research are to improve our understanding of the processes controlling metal-ion adsorption and to explain the magnitude of dispersion of reactive species observed in ground-water transport.

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investigating the spatial structure of the variability in adsorption and hydraulic conductivity and the correlations among these properties is one part of this research. In this paper, we report initial results of our investigation of spatial variability in zinc adsorption (Zn-ads) and lead adsorption (Pb-ads) and hydraulic conductivity in a sand and gravel aquifer on Cape Cod, Massachusetts. This research is supported by the R. S. Kerr Environmental Research Laboratory of the U.S. Environmental Protection Agency and the U.S. Geological Survey (USGS) Toxic Substances Hydrology Program.

This study was conducted using sediments collected at the USGS Toxic Substances Hydrology Research Site on Cape Cod, Massachusetts (fig. 1). The aquifer at the site is shallow, unconfined, and composed of glacial-outwash sediments. The unconsolidated sediments consist predominately of medium to coarse sand, interbedded with gravel and fine sand. Typically less than 1 percent of the sediments are fine grained (less than 0.0625 mm size fraction), and the amount of sedimentary organic carbon is less than 0.1 percent by dry weight (Barber and others, 1992). The aquifer has an average porosity of 0.39; average ground-water velocity within the aquifer is 0.4 m/d (LeBlanc and others, 1991).

The cores were collected in the vicinity of the array of multilevel samplers (fig. 1) that was installed for a large-scale, natural-gradient tracer test conducted during 1985-88 to investigate macrodispersion in the aquifer (Garabedian and others, 1991; LeBlanc and others, 1991; Stollenwerk, 1987). This array is currently being used to investigate the transport of lead and zinc, as well as other reactive and nonreactive solutes, in a second large-scale test (Davis and others, 1995, this proceedings). Variability in \( K \) was previously investigated at this site by use of permeameter tests of cores (Wolf and others, 1991) and flowmeter tests conducted in long-screened wells (Hess and others, 1992).

METHODS

In this study, 14 continuous cores of subsurface material (fig. 1) were collected from the sand and gravel aquifer. These cores were analyzed in the laboratory for grain-size distribution and adsorption properties.

Core Collection

Cores were collected from an approximate vertical interval of 4 m. Individual cores were up to 1.5 m long and 5 cm in diameter. Cores were collected in plastic core liners using a wireline-piston core barrel (Zapico and others, 1987). As many as four cores were collected in each of the 14 boreholes. Cores were frozen until analyzed. Cores were collected from eight boreholes positioned 1 to 4 m apart along a 16-m-long transect (fig. 1) oriented approximately parallel to the current direction of ground-water flow and the general paleodirection of the flow of the streams that deposited the outwash sediments. These transect cores were used to assess spatial correlation of metal-ion adsorption and \( K \).

Additional widely spaced cores were collected from six boreholes (fig. 1), positioned an average of 30 m apart, to analyze variability in geochemical and hydrologic properties and to assess how representative the transect cores are of a larger portion of the aquifer (spatial stationarity within the aquifer properties).

Laboratory Analyses

Each core was sectioned into subsamples approximately 10 cm long for laboratory analysis. Samples were dried in a laminar-flow hood and sieved to remove grains larger than 1 mm in diameter. The less-than-1 mm fraction was then divided into two parts with a riffle splitter. One part was used for batch adsorption experiments; the other part was used for grain-size analysis. The largest fraction was removed to reduce the possibility of obtaining nonrepresentative subsamples for the batch experiments.

Grain-size distributions on the less-than-1 mm fraction were determined using a dry-sieve analysis in the USGS Sediment Laboratory in Harrisburg, Pa. The weight of the greater-than-1 mm fraction was included in the final grain-size data set. Wolf and others (1991) reported agreement between \( K \) calculated from grain-size distributions using the relation developed by Hazen (1893) and \( K \) measured in permeameter tests of cores from this site. Therefore, Hazen's relation was used to estimate \( K \) values for the samples in this investigation --

\[
K = A (d_{10})^2.
\]
where $K$ is hydraulic conductivity, in cm/s at 10 °C; $A$ is a constant to correct for temperature (1.157 cm/(s mm$^2$) at 10 °C); and $d_10$ is the grain diameter, in mm, that is larger than 10 percent of all the grains in the sample, by weight (10th percentile).

Lead and zinc adsorption were measured in batch experiments using aquifer samples and artificial ground water. Fuller and others (1996) and Davis and others (1994) report detailed methodologies for these experiments.
SUMMARY OF LABORATORY RESULTS

Figure 2 presents the estimated $K$ values for core F415C38 (see fig. 1 for location) and illustrates the variability of $K$ values. Estimates of $K$ were made for 375 sediment samples. The geometric mean $K$ of 0.073 cm/s (table 1) is only slightly less than the mean of 0.1 cm/s reported by Hess and others (1992) based on borehole flowmeter tests, and by LeBlanc and others (1991) based on a large-scale tracer test at this site. The variance of the natural logarithm of $K$ ($\text{ln} K$) of 0.138 is similar to that reported by Hess and others (1992) based on the permeameter tests conducted on cores from this site. This variance is slightly less than the variance of 0.24 reported for the flowmeter tests (Hess and others, 1992). If only the 268 samples from the transect are considered, the mean is 0.071 cm/s and the variance is 0.141. The similarities between the mean and variance of the hydraulic conductivities of the transect cores and those of all cores suggest that the transect cores represent a larger portion of the aquifer than that covered by the transect cores and that spatial stationarity may exist in the $K$ distribution.

A total of 374 and 371 samples were analyzed for lead and zinc adsorption, respectively. Results of the adsorption batch experiments for core F415C38 are shown in figure 2 of Fuller and others (1996). Results are reported in micromoles of solute adsorbed per gram of sediment ($\mu\text{mol/g}$) at a pH of 5.3 and a sand-to-water ratio of 50 g/L. The mean Pb-ads of 0.225 $\mu\text{mol/g}$ is significantly greater than the mean Zn-ads of 0.011 $\mu\text{mol/g}$ (table 1). This result was expected because lead has a greater affinity for surfaces than does zinc. However, the variance of the Zn-ads data is unexpectedly greater than that of the Pb-ads data. As is the case with the $K$ data, spatial stationarity in the adsorption-data sets is suggested if the transect results are compared to results from all cores.

<table>
<thead>
<tr>
<th>Number of values</th>
<th>Hydraulic conductivity</th>
<th>Lead adsorption</th>
<th>Zinc adsorption</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(centimeters per second)</td>
<td>(micromoles per gram)</td>
<td>(micromoles per gram)</td>
</tr>
<tr>
<td>Minimum</td>
<td>.007</td>
<td>.091</td>
<td>0</td>
</tr>
<tr>
<td>Maximum</td>
<td>.261</td>
<td>.371</td>
<td>.028</td>
</tr>
<tr>
<td>Geometric mean</td>
<td>.073</td>
<td>.225</td>
<td>.011</td>
</tr>
<tr>
<td>Variance of natural logarithm</td>
<td>.138</td>
<td>.019</td>
<td>.212</td>
</tr>
</tbody>
</table>

The data sets are truncated at zero and positively skewed, suggesting that the data are lognormally distributed. The log-normality of $K$ is widely accepted (Freeze, 1975); the lognormal nature of the adsorption data is speculated here. A rigorous test of normality is not attempted here because of the correlated nature of the data sets and the limited amount of data.

Correlations Among Aquifer Properties

A significant positive correlation is found between zinc and lead adsorption (table 2). Fuller and others (1996) and Davis and others (1994) describe the mineral-surface properties that control the adsorption of these metal ions; they attribute the zinc and lead adsorption variability to variability in the surface area and the composition of the metal-oxide coatings on the sediment grains.
Table 2. Pearson correlation coefficients between hydraulic conductivity, lead adsorption, and zinc adsorption

[P-values are reported in parentheses. P-values greater than 0.05 are considered statistically insignificant]

<table>
<thead>
<tr>
<th></th>
<th>Hydraulic conductivity</th>
<th>Lead adsorption</th>
<th>Zinc adsorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydraulic conductivity</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lead adsorption</td>
<td>-0.291 (0.0001)</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Zinc adsorption</td>
<td>-0.086 (0.097)</td>
<td>0.515 (0.0001)</td>
<td>1</td>
</tr>
</tbody>
</table>

A negative correlation between adsorption and $K$ has been suggested as a contributor to the enhanced dispersion of reactive solutes observed in the field relative to the dispersion of nonreactive solutes (Garabedian and others, 1988); that is, zones of low $K$ may have greater adsorption capacities that increase dispersion of the reactive species. The dependence of the metal-ion adsorption data on the $K$ data measured in this investigation is shown in figure 3. A statistically significant, but small, negative correlation is identified for Pb-ads and $K$ (table 2). However, a statistically insignificant ($p > 0.05$) negative correlation is calculated for Zn-ads and $K$. The greater variance in the Zn-ads data compared to that in the Pb-ads data is shown in figure 3.

Spatial Variability of Aquifer Properties

A geostatistical analysis allows quantification of the spatial correlation structure of discrete spatial data (Journel and Huijbregts, 1978). The basic tool of the analysis is the experimental semivariogram, which is calculated as the mean-squared differences between sample values at specific separation distances--

$$\gamma(h) = \frac{1}{2n(h)} \sum_{i=1}^{n(h)} [y_i - y_{i+k}]^2,$$

where $\gamma$ is the semivariogram, $h$ is the mean separation distance between observations, $n(h)$ is the number of data pairs separated a distance $h$, and $y_i$ is the spatially distributed data being analyzed. In practice, the semivariogram is constructed so that $h$ is the mean distance between points within a range of distances, known as a lag class. Data exhibiting spatial correlation will have variogram values that are small at small separation distances and that increase to an asymptotic value equal to the variance of the data set at greater distances.

Variogram analyses were made on data from the transect cores to characterize spatial correlation within the hydraulic-conductivity and adsorption data sets. Variograms were constructed in the vertical and

![Graph showing relation between lead and zinc adsorption determined from batch experiments and hydraulic conductivity estimated from grain-size data.](image)
horizontal directions along the transect. This transect is about 6 m from and approximately parallel to the transect of cores and boreholes used by Hess and others (1992) to characterize correlation within the hydraulic-conductivity distribution in this aquifer. The variogram analyses were conducted with the natural-logarithm transforms of data (lnK, lnPb-ads, and lnZn-ads) for the 268 transect core samples.

In the variogram analyses, the lag classes were based on the sample spacing. In the vertical direction, samples were, on average, 0.1 m long, and sampling was usually continuous within boreholes. Therefore, the minimum lag in the vertical direction was set equal to 0.1 m. Each lag-class calculation included at least 100 data pairs in the vertical direction.

In the horizontal direction, sampling was not continuous and was limited to discrete boreholes. The minimum spacing between boreholes was approximately 1 m; a mean distance of 1.4 m was used for the smallest lag in the horizontal semivariograms to ensure a minimum of 50 data pairs in each lag class. Vertical semivariograms are better defined than horizontal semivariograms because of the continuity in sampling in the vertical direction and the discontinuity in sampling in the horizontal direction.

A negative-exponential form was chosen to model the experimental semivariograms:

\[ Y(h) = s^2 \left[ 1 - e^{-h/\lambda} \right], \quad (3) \]

where \( y \) is the variogram, \( s^2 \) is the variogram sill, \( h \) is the separation distance between data points, and \( \lambda \) is the correlation scale. The sill is the asymptote to which the model approaches as the separation distance increases. The correlation scale is a length over which the data display significant spatial correlation. Both the sill and the correlation scale can be varied to fit the model to the experimental semivariograms. The sill is typically set to approximately the sample variance; the correlation scale is, therefore, the primary model parameter to be determined through fitting the model to the experimental semivariogram. This scale controls the rise of the model to the asymptote and quantifies the spatial correlation of the data.

The vertical semivariograms show greater correlations (smaller variogram values) at smaller separation distances than at larger distances. The vertical semivariogram for lnZn-ads is shown in figure 4. The vertical correlation scales identified by the fitted models are 0.1, 0.15, and 0.26 m for lnK, lnPb-ads, and lnZn-ads, respectively. These values are similar to the vertical correlation scales for lnK (0.18-0.38 m) identified by Hess and others (1992). The differences in vertical correlation scale reported here are probably not significant considering that \( K \) was estimated on the basis of grain-size distribution and that the laboratory determinations of adsorption were made with some degree of error (see fig. 2 in Fuller and others, 1996). The similarity in vertical correlation scales for lnK, lnPb-ads, and lnZn-ads is interesting and warrants further investigation; however, the similarity in correlation scales does not necessarily imply causality.

The horizontal semivariograms show a lack of correlation at all separation distances investigated (1.4 to 12 m). Therefore, no models were fit to these horizontal semivariograms. Hess and others (1992) reported horizontal scales for lnK of 2.9 to 8 m for this site. Horizontal scales could not be resolved in this study for lnK, as well as for the adsorption data sets, suggesting that the horizontal sampling density at small separation distances was not adequate to resolve small-scale correlation. Additional data may be necessary to determine the horizontal correlation scales of the adsorption properties.

CONCLUSIONS

More than 370 laboratory batch experiments show that lead and zinc adsorption vary significantly within the sand and gravel aquifer on Cape Cod, Massachusetts. A statistically significant, but small negative correlation between lead adsorption and hydraulic conductivity was observed. This type of correlation could explain, in part, enhanced dispersion of reactive species observed in the field relative to the dispersion of nonreactive solutes. The correlation between zinc adsorption and hydraulic conductivity, however, is not statistically significant. Vertical correlation scales determined for metal-ion adsorption are similar to those determined for hydraulic conductivity in this and previous studies. Finally, horizontal correlation scales could not be resolved for the adsorption and hydraulic-conductivity data sets, possibly because of the large horizontal spacing between data used in this study.
Figure 4. Vertical semivariogram of the natural logarithm of the zinc adsorption data from the eight transect cores (locations shown on fig. 1). The point values are the experimental semivariogram (eq. 2); the solid line is the negative-exponential model (eq. 3) fit to the experimental semivariogram. The model fit has a sill value of 0.17 and a correlation scale of 0.26 meters.

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Small-Scale Tracer Tests Applied to the Measurement of \textit{in situ} Denitrification Rates in a Sewage-Contaminated Aquifer, Cape Cod, Massachusetts

By Myron H. Brooks\textsuperscript{1}, Richard L. Smith\textsuperscript{1}, and Stephen P. Garabedian\textsuperscript{2}

Abstract

Small-scale natural-gradient tracer tests were used to measure \textit{in situ} rates of denitrification in a nitrate-contaminated aquifer. Tracer solutions contained bromide, a conservative tracer, and acetylene, an inhibitor of nitrous oxide reductase. Breakthrough of the tracer solution and production of nitrous oxide were monitored at multilevel samplers approximately 10 meters downgradient from the injection multilevel sampler for a period of up to 40 days. Calculated rates of denitrification from two tracer tests were 620 and 410 nanomoles N\textsubscript{2}O per liter of aquifer per day. These rates are on the low end of the range of reported rates in aquatic sediments, and are similar, but lower than, previous rate measurements made at the Cape Cod site by using flask and whole-core incubation techniques. Results of this study suggest that incubation techniques using aquifer sediments might slightly overestimate \textit{in situ} denitrification rates in ground water. Peak concentrations of nitrous oxide lagged 2 days behind the peak concentrations of the conservative tracer in both tests. Work is currently underway to examine possible mechanisms for this result, and to model it by using a modified one dimensional advection-dispersion model containing a Michaelis-Menten term for nitrous oxide production.

INTRODUCTION

Nitrate (NO\textsubscript{3}\textsuperscript{−}) is one of the most widespread contaminants in shallow ground water in North America and Europe (Gillham and Cherry, 1982). Nitrate is an undesirable byproduct of numerous activities including fertilizer application, livestock production, and sewage treatment, and tends to be persistent in ground water despite its predicted instability at near neutral pH (Howard, 1985). This persistence is a problem if the NO\textsubscript{3}\textsuperscript{−}-contaminated aquifer is a source of drinking water. Elevated concentrations of NO\textsubscript{3}\textsuperscript{−} in drinking water can cause methemoglobinemia in infants (Comley, 1945), and have been implicated in the increased incidence of cancer (Jensen, 1982) and hypertension (Morton, 1971) in adults. Concern over the increased frequency of ground-water contamination by NO\textsubscript{3}\textsuperscript{−} has heightened interest in techniques that remove NO\textsubscript{3}\textsuperscript{−} from ground water. One remediation technique uses biological denitrification, a process carried out by bacteria in which NO\textsubscript{3}\textsuperscript{−} can serve as an electron acceptor and can ultimately be reduced to dinitrogen (N\textsubscript{2}). The reduction proceeds stepwise from NO\textsubscript{3}\textsuperscript{−} through nitrite (NO\textsubscript{2}\textsuperscript{−}), nitric oxide, and nitrous oxide (N\textsubscript{2}O) to N\textsubscript{2}; each step is catalyzed by a separate enzyme. Geochemical evidence from several studies has indicated that denitrification occurs in ground water (Gillham and Cherry, 1978; Edmunds and Walton, 1983). Measurements of denitrification rate have been made indirectly by using incubations with aquifer core material (Slater and Capone, 1987; Smith and Duff, 1988; Smith and others, 1991a). In one study, denitrification was directly measured \textit{in situ} (Trudell and others, 1986) by using a drive point to inject, and then sample, a NO\textsubscript{3}\textsuperscript{−} containing tracer solution in a denitrifying zone approximately 3 m below land surface.

Remediation of NO\textsubscript{3}\textsuperscript{−} contamination employing denitrifying bacteria has been attempted using both “pump and treat” (van der Hoek and Klapwijk, 1987) and \textit{in situ} techniques (Mateju and others, 1992). \textit{In situ} remediation using denitrification is particularly attractive because the ultimate product (N\textsubscript{2}) is harmless. Most proposed \textit{in situ} remediation plans involve stimulating existing populations of denitrifying bacteria...
through the addition of carbon substrates. Although there have been successes with this approach (Mateju and others, 1992), little is known about the native bacterial populations that are used to catalyze the reduction of \( \text{NO}_3^- \) or the physical and chemical factors that control their activity in situ. Information of this type will be of value to scientists and engineers designing \( \text{NO}_3^- \) remediation programs that use biological denitrification. The purposes of this study were to test the feasibility of using small-scale natural-gradient tracer tests to quantify denitrification rates in a nitrate-contaminated aquifer, and to compare those rates to previously measured rates obtained by using aquifer core material incubated in flasks in the laboratory. Acetylene (\( \text{C}_2\text{H}_2 \)), an inhibitor of nitrous oxide reductase (the enzyme that catalyzes the reduction of \( \text{N}_2\text{O} \) to \( \text{N}_2 \)), was added to a ground-water solution containing a conservative tracer that was injected into a zone of active denitrification at the Cape Cod study site. Subsequent production of \( \text{N}_2\text{O} \) was monitored downgradient, and the \( \text{N}_2\text{O} \) produced was used to calculate an in situ rate of denitrification. The results of these experiments represent new information about the denitrification process in ground water and provide insight into the functioning of one of the enzymes that catalyzes the process. The purpose and scope of this paper are to describe the results of the tracer test experiments and to compare these results with other studies of ground-water contamination.

**MATERIALS AND METHODS**

**Study Site**

The study site is a shallow sand and gravel aquifer located on Cape Cod, Mass. Contamination at this site is the result of more than 50 years of land disposal of secondarily treated sewage (LeBlanc, 1984). Natural-gradient tracer tests were performed at site F473 (fig. 1), which consists of an array of 21 multilevel samplers, each having 15 evenly spaced (vertical spacing = 25 cm) sampling ports at altitudes of 8.56 to 12.09 m above sea level. One sampler located upgradient of the remaining 20 (F473M0-11) served as the injection sampler. The remaining samplers were arranged in three rows approximately 4, 7, and 10 m downgradient of the injection sampler; each row was aligned roughly perpendicular to the direction of ground-water flow (fig. 1).

**Tracer Injection and Sampling**

Small-scale natural-gradient tracer tests were performed in May and June 1991 and August and September 1992. Approximately 100 L of ground water was withdrawn from a single sampling port in the injection multilevel sampler by using a peristaltic pump outfitted with gas impermeable tubing. The sampling port, located 10.08 m above sea level, was located within a previously identified zone of active denitrification. The ground water was pumped into a gas impermeable bladder that had been flushed seven times with \( \text{N}_2 \). The bladder contained 12.88 g of sodium bromide that had been dissolved in approximately 1 L of anoxic, distilled water. Several liters of \( \text{C}_2\text{H}_2 \) were added to the headspace in the bladder and allowed to equilibrate for 1 hour to create a saturated solution of this highly soluble gas. Undissolved \( \text{C}_2\text{H}_2 \) was then vented from the bladder and the injectate solution was pumped back down the injection sampler port from which it was originally taken. The pumping rate for the injection was approximately 1.4 L per minute. Samples of the injectate solution were taken at the outset, approximate halfway point, and end of the injection period for \( \text{NO}_3^- \), \( \text{NO}_2^- \), \( \text{Br}^- \), \( \text{N}_2\text{O} \), and \( \text{C}_2\text{H}_2 \). Samples for these constituents were then collected daily for 33 days (1991) and 40 days (1992) at selected multilevel samplers downgradient to monitor the production of \( \text{N}_2\text{O} \) as the tracer cloud moved through the aquifer. Samples (60 mL) for analysis of \( \text{NO}_3^- \), \( \text{NO}_2^- \), and \( \text{Br}^- \) concentrations were filtered in the field (0.45 \( \mu \text{m} \)). Samples for analysis of \( \text{NO}_3^- \) and \( \text{NO}_2^- \) were preserved by freezing. Samples for \( \text{Br}^- \) analysis were normally analyzed on the day of collection. Samples for \( \text{N}_2\text{O} \) and \( \text{C}_2\text{H}_2 \) analyses were collected in 20-mL plastic syringes using positive pressure supplied by the peristaltic pump. A 22-gauge needle was then attached to the syringe and 15 mL of sample was injected through the stopper of a 30-mL serum bottle. Prior to sample introduction, the serum bottles received 200 \( \mu \text{L} \) of 12.5 N \( \text{NaOH} \) to eliminate biological activity, were capped with butyl rubber stoppers, and crimp sealed.

**Analytical Techniques**

\( \text{Br}^- \) was analyzed by ion selective electrode. \( \text{NO}_3^- \) and \( \text{NO}_2^- \) were determined colorimetrically by using a flow-injection autoanalyzer. \( \text{N}_2\text{O} \) and \( \text{C}_2\text{H}_2 \) were analyzed by gas chromatographic headspace analysis. \( \text{N}_2\text{O} \) was quantified with an electron capture detector; \( \text{C}_2\text{H}_2 \) was quantified with a flame-ionization detector. Concentrations in water were calculated from the headspace concentrations by using empirical solubility relationships.
RESULTS AND DISCUSSION

The composition of tracer solutions for the 1991 and 1992 experiments is shown in table 1. With the exception of the variation in the contaminant NO_3 concentration, the composition of the two tracer solutions was virtually identical for the two experiments. The mass of NaBr (12.88 g) added to the injectate solution was calculated to produce a 100 ppm Br⁻ solution if brought to a final volume of 100 L. Observed injectate Br⁻ concentrations can be used to calculate the actual volume of tracer solution for each test; they were 124.6 L in 1991 and 119.3 L in 1992.

Breakthrough curves of Br⁻, C_2H_2, and N_2O for the 1991 and 1992 experiments at multilevel sampling ports approximately 10 m downgradient from the...
### Table 1. Injectate solution composition for small-scale natural-gradient tracer tests performed at site F473, May and June 1991 and August and September 1992 [ppm, parts per million]

<table>
<thead>
<tr>
<th>Year</th>
<th>Bromide (ppm)</th>
<th>Acetylene (millimoles per liter)</th>
<th>Nitrous oxide (micromoles per liter)</th>
<th>Nitrate-N (ppm)</th>
<th>Nitrite-N (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1991</td>
<td>79.4</td>
<td>6.1</td>
<td>9.17</td>
<td>15.3</td>
<td>0.53</td>
</tr>
<tr>
<td>1992</td>
<td>83.0</td>
<td>6.2</td>
<td>9.16</td>
<td>24.2</td>
<td>.42</td>
</tr>
</tbody>
</table>

Maximum breakthrough was not observed at the same sampler for the two tests. The curves in figure 2 for the 1991 experiment were constructed from data collected at sampling site F473M6-13 (fig. 1). The curves for the 1992 experiment were constructed from data collected at sampling site F473M6-15 (fig. 1). The sampling port where maximum breakthrough occurred in the 1991 was also 25 cm lower than the sampling port where maximum tracer breakthrough in the 1992 experiment was observed. Travel distance from the injection port to the sampling port was about 9.5 m in the 1991 experiment and about 10.5 m in the 1992 experiment.

Dimensionless breakthrough curves (observed concentration divided by injectate concentration) for Br⁻ and C₂H₂ were virtually identical in each test (figs. 2 and 3). C₂H₂ was added as an inhibitor of nitrous oxide reductase, but it also functioned as a second conservative tracer. Maximum concentrations of Br⁻ and C₂H₂ occurred 21 days after injection in 1991 (fig. 2), and 28 days after injection in 1992 (fig. 3). More of the tracer was recovered in 1992 (peak dimensionless concentration = 0.41) than in 1991 (peak dimensionless concentration = 0.24). Differences in travel times and maximum conservative tracer concentrations observed for the two tracer tests are most likely related to a slight difference in hydraulic gradient that existed between the two experiments.

N₂O production was similar for both tests. The peak N₂O concentration in 1991 was 42.5 μm, whereas the peak concentration observed in 1992 was 38.9 μm. Background N₂O concentrations were similar for both experiments (table 1, figs. 2 and 3). Maximum denitrification rates were calculated by dividing the amount of N₂O produced (peak concentration minus the injectate

**Figure 2.** Breakthrough curves of bromide, acetylene, and nitrous oxide at one multilevel sampling port at sampler F473M6-13 for an acetylene-block natural-gradient tracer test performed during May and June 1991. Bromide and acetylene values are normalized to the injectate concentration.

**Figure 3.** Breakthrough curves of bromide, acetylene, and nitrous oxide at one multilevel sampling port at sampler F473M6-15 for an acetylene-block natural-gradient tracer test performed during August and September 1992. Bromide and acetylene values are normalized to the injectate concentration.
concentration) by the number of days from injection until the maximum N\textsubscript{2}O concentration was observed and then correcting for the average porosity of the aquifer. Rates for the two experiments were 620 nmol N\textsubscript{2}O \cdot (L aquifer)\textsuperscript{-1} \cdot d\textsuperscript{-1} in 1991 and 410 nmol N\textsubscript{2}O \cdot (L aquifer)\textsuperscript{-1} \cdot d\textsuperscript{-1} in 1992. These rates, which are a first approximation of actual \textit{in situ} rates because they do not account for dispersion, represent the lower end of reported denitrification rates from aquatic sediments (Knowles, 1982). The calculated rates are similar to, but lower than, rates measured previously at the Cape Cod site by use of flask and whole core incubation techniques (Smith and Duff, 1988; Smith and others, 1991), suggesting that these techniques may slightly overestimate \textit{in situ} rates. The larger of the two rates measured in this study would completely remove 14 mg N/L NO\textsubscript{3} from the aquifer in 314 days if the process were a zero order reaction at all NO\textsubscript{3} concentrations. This is in contrast to the results of \textit{in situ} experiments performed by Trudell and others (1986). In that study, a tracer solution containing 13 mg N/L NO\textsubscript{3} was injected into a zone containing virtually no NO\textsubscript{3}, and enough NO\textsubscript{3} was denitrified within 356 hours so that the NO\textsubscript{3} lost could be measured directly. The authors reported an increase in bicarbonate that was in stoichiometric agreement with the predicted amount for heterotrophic denitrification, and noted that organic carbon present in the aquifer was adequate to denitrify large amounts of NO\textsubscript{3} in the aquifer. At the Cape Cod site, ground water containing 15 to 24 mg N/L NO\textsubscript{3} was present in the zone where the experiment was performed, and previous work had demonstrated that denitrification there was limited by the lack of available organic carbon (Smith and Duff, 1988). The amount of NO\textsubscript{3} denitrified in 672 hours was detectable only because of the increased analytical sensitivity provided by the acetylene-block technique; NO\textsubscript{3} concentrations in the tracer clouds were unchanged during the experiments (data not shown).

In both tracer tests the peak N\textsubscript{2}O concentrations occurred 2 days after the peak conservative tracer concentrations occurred (figs. 2 and 3). Attempts to model these results using a modified one-dimensional advection-dispersion model containing a Michaelis-Menten term for N\textsubscript{2}O production have been unsuccessful at replicating the timing and shape of the N\textsubscript{2}O breakthrough curves. The modeling approach being used is similar to the one used by Smith and others (1991b) to simulate a consumption process (methane oxidation) during similar natural-gradient tracer experiments at the Cape Cod site. One possible explanation for the lag between the peaks of the conservative tracer breakthrough curves and the N\textsubscript{2}O breakthrough curves is that nitrous oxide reductase binds N\textsubscript{2}O in the presence of C\textsubscript{2}H\textsubscript{2}. An early paper on the acetylene-block phenomenon reported that the inhibition was noncompetitive (Yoshinari and others, 1976), indicating that the mechanism of inhibition does not involve C\textsubscript{2}H\textsubscript{2} binding to the active site of the enzyme. If N\textsubscript{2}O did bind to all available enzyme active sites as the tracer cloud moved through the aquifer, no net N\textsubscript{2}O production would occur until all of the active sites of nitrous oxide reductase in both attached and free-living bacteria were saturated with N\textsubscript{2}O. This could result in the breakthrough curve characteristics observed in the two tests.

Laboratory experiments with a denitrifying pure culture are being conducted to test this hypothesis. If this phenomenon can be demonstrated, an attempt will be made to incorporate it into the modified advection-dispersion model.

**SUMMARY**

The feasibility of measuring ground-water denitrification rates \textit{in situ} by using natural-gradient tracer tests was demonstrated. Br\textsuperscript{−} was used as the conservative tracer and C\textsubscript{2}H\textsubscript{2} was added to inhibit the activity of nitrous oxide reductase. Production of N\textsubscript{2}O was monitored at downgradient sampling ports, and the N\textsubscript{2}O produced as the tracer cloud moved through the aquifer was used to calculate an \textit{in situ} denitrification rate. Rates from replicate experiments were similar and in the low end of the range of rates reported for soils and aquatic sediments. The rates were similar to rates reported previously for the Cape Cod site in studies that employed flask and whole core incubation techniques. The shape and timing of N\textsubscript{2}O breakthrough curves relative to the conservative tracers was different than expected. It is hypothesized that this result may be related to the noncompetitive inhibition of nitrous oxide reductase by C\textsubscript{2}H\textsubscript{2}. Experiments are underway to test this hypothesis, and to model this result using a modified one-dimensional advection-dispersion model containing a Michaelis-Menten term for N\textsubscript{2}O production.
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Overview of Research on the Distribution and Role of Protozoa in an Organically Contaminated Aquifer at Cape Cod, Massachusetts

By Nancy E. Kinner¹ and Ronald W. Harvey²

Abstract

The distribution, nature, and role of protozoa that inhabit contaminated and uncontaminated ground water were investigated at the U.S. Geological Survey (USGS) Cape Cod Toxic-Substances Hydrology Research Site. New information has included identification of large protozoan populations (up to $10^5$/gram dry weight) in anoxic zones of the aquifer; a lack of correlation between dissolved oxygen concentrations and protozoan abundance or degree of encystment; a strong relation among concentrations of dissolved organic carbon, phosphate, sulfate, nitrate, numbers of free-living bacteria (FLB) and protozoa; and a ratio of FLB to protozoa that is 10-100 times lower than that typically found in other aqueous environments. An improved direct-counting procedure has allowed more accurate enumeration of protozoa in sandy, aquifer sediments than was previously possible.

INTRODUCTION

In 1987, protozoa were found at a variety of locations in the contaminant plume at the U.S. Geological Survey (USGS) Cape Cod Toxic-Substances Hydrology Research Site (fig. 1). In 1990, the National Science Foundation (NSF) funded a 3-year study (NSF Grant # BCS 9012183 awarded to the University of New Hampshire) involving the distribution and role of the protozoa in the aquifer. This paper presents an overview of the preliminary results obtained during this collaborative project between the University of New Hampshire, the USGS, and the Natural History Museum (London).

METHODS

A new application of epifluorescent direct counting was used to enumerate 4',6-diamidino-2-phenylindole (DAPI)-stained protozoa recovered from core material. Estimates of the number of protozoa present based on use of the epifluorescent method were comparable to those based on use of the Darbyshire liquid media most-probable-number (MPN) technique (Darbyshire and others, 1974), but differed from those of the Singh solid-media MPN method (Singh, 1946). Both the Darbyshire and Singh methods were originally developed for enumeration of protozoa in topsoil and recently have been applied to subsurface samples. During the Cape Cod protozoa study, the epifluorescent technique has been used because it has the advantages of low counting variability and avoids media/culturing selectivity. However, all cores also have been analyzed by the Darbyshire method because that method gives an indication of the percentage of the protozoan population that is encysted.

RESULTS AND DISCUSSION

A survey of the aquifer was conducted to determine the distribution of protozoa throughout the 4.5-km long plume of sewage-contaminated ground water that originates at Otis Air Base (fig. 1). Cores...
and porewater samples were collected at a pristine control site and along longitudinal (12 sites) and vertical (3 sites with 4-5 depths per site) transects through the plume. In oxic and anoxic zones in the contaminant plume, protozoan abundance typically varied between $10^4$ and $10^5$ gw (gram dry weight) sediment with 3 to 40 percent of the population encysted. In the alkylbenzene sulfonate (ABS)-contaminated part of the plume and at the pristine site, protozoan abundance was lower ($10^{-1}$-$10^4$ gw). There was no correlation between dissolved oxygen (DO) concentration and protozoan abundance or percent...
encystment, indicating that the protozoa are not excluded from anoxic regions of the aquifer as was once believed. Indeed, their numbers are relatively high within the non-ABS parts of the plume. Consistently, more than 70 percent of the population appears to be trophic, suggesting that protozoa may play an active role in the microbial community of the contaminant plume. More than 99 percent are small flagellates (2-3 μm in length). Few amoebae and no ciliates were detected.

Principal component factors were used to assess significant multivariate relations among biogeochemical characteristics of the plume and the protozoan population. There was a strong relation among the variables dissolved organic carbon (DOC), PO₄³⁻, SO₄²⁻, NO₃⁻, FLB and protozoa. This relation indicated that protozoa and FLB may be using DOC (less than 0.45 m filtration fraction). Although a relation between DOC and FLB was expected and shown previously for the Cape Cod site (Harvey and Barber, 1992), the direct relation between protozoa populations and DOC concentration was surprising. There was only a limited inverse relation between the populations of FLB and protozoa indicating a weak predator-prey relation. The ratio of FLB to protozoa at each site in the plume ranged from 10¹ to 10²; normally this ratio is ~10² in aqueous environments when protozoa are preying on FLB (Fenchel, 1987). The survey data suggest the aquifer protozoa (2-3 μm) are either feeding on high-molecular-weight DOC directly and (or) on a limited size range of FLB.

When the NSF grant was written in 1989, it was assumed that protozoa would have a role in the organically contaminated subsurface similar to the one they play in most other environments as predators upon bacteria. As predators upon FLB, protozoa have been shown to have a positive effect on bacterial degradation of organic compounds in aqueous and topsoil ecosystems because they release nutrients and cytoplasmic constituents necessary for bacterial growth and they keep bacterial numbers low and in the exponential growth phase. In order to explore the potential predator-prey relation, laboratory columns (10 cm long) containing established communities of attached bacteria (10⁶-10⁷/gdw) and 2 to 3 μm protozoa (10⁴-10⁵/gdw) from the Cape Cod site were fed an injectate containing DAPI-stained, cultured bacteria (10⁵ cells/mL, 1 μm cell length) that were isolated from the aquifer. The injectate also contained carboxylated microspheres (1.5-1.7 μm diameter) and a conservative tracer (bromide, 20 mg/L). There was also a population of unstained FLB (10⁶ cells/mL) present in the injectate. A similar injection was repeated after the column was sterilized. Fewer DAPI-stained FLB were expected to elute from the column (C_Cout/C_Cin) in the protozoa-populated (nonsterile) column because of predation. However, this was not observed and is again in agreement with the theories of Fenchel (Fenchel, 1986 and 1987) that the size ratio of protozoa:FLB must be on the order of 10:1 for predation to occur. In the column studies, this size ratio was less than 5:1. As with the survey data, these results suggest that the 2 to 3 μm protozoa in the plume may be (1) selectively grazing on small FLB (0.2 to 0.3 μm), most of which exist within the first 0.08 km of the plume (Harvey and Garabedian, 1991); and (or) (2) directly using high-molecular-weight DOC.

In experiments currently being conducted at the Cape Cod site, flow-through incubation chambers (100,000 molecular-weight cutoff, sterile dialysis membranes) are being used to study the relation between protozoa and FLB. Controls in these experiments include membranes containing sterile water and DAPI-stained glutaraldehyde-fixed (killed) aquifer FLB. Initial chamber tests using 0.8 to 1 μm ground-water isolates suggest an equilibrium abundance or carrying capacity of ~10⁶ FLB/mL porewater. In separate experiments, initial stocks of FLB (10⁴, 10⁵, 10⁷ cells/mL) converged to ~10⁶ cells/mL after 1 week in situ incubations. Interestingly, this is similar to the abundance of FLB found in situ in the area of the contaminant plume (F513, 0.45 km downgradient from the sewage treatment plant) where the study is being conducted (Harvey and Barber, 1992). Subsequent experiments now being conducted involve in situ incubations of aquifer protozoa and FLB. In these experiments, population changes are being monitored over time. Comparison of these results with those of bacteria alone will help determine if there is an interaction between the aquifer FLB and protozoa.

ACKNOWLEDGMENTS

We thank D.M. Shay, C.A. Gruden, A.L. Bunn, and M. Kazmierkiewicz-Tabaka of the University of New Hampshire (Durham, New Hampshire) for their laboratory work with protozoa. We also thank David Metge, Larry Barber and Richard Smith (USGS;
Boulder, CO), respectively, for their analyses of bacteria, DOC, and ammonia samples and the New England District Office of the USGS for their logistical support.

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Transport of Indigenous Protozoa in a Sandy Aquifer, Cape Cod, Massachusetts

By Ronald W. Harvey¹, Nancy E. Kinner², Dan MacDonald², Amoret L. Bunn², and David W. Metge¹

Abstract

Transport of flagellates in sandy, organically contaminated aquifer sediments was investigated in a small-scale (2 m travel distance) natural-gradient tracer test in Cape Cod. The flagellates (average cell size, 2-3 μm), which appear to be common in the Cape Cod aquifer, were grown in Cerophyl, labeled with hydroethidine (a vital eukaryotic stain), and coinjected into aquifer sediments along with a conservative tracer (bromide). Rates of immobilization in undisturbed aquifer sediments were more than two orders of magnitude greater than those observed earlier for indigenous ground-water bacteria. The high rate of immobilization appeared to be related to the surface chemistries of the flagellates and not their size. Retardation for the flagellates was two- to three-fold greater than that generally observed for indigenous groundwater bacteria. Apparent dispersion was also significantly greater for the flagellates than for the bacteria and was much closer to that observed earlier for highly surface-active, microbial-sized, carboxylated-latex microspheres. The data suggest that flagellates are probably transported slowly through the aquifer.

INTRODUCTION

The goals of the protozoa research program at the U.S. Geological Survey (USGS) Cape Cod Toxic-Substances Hydrology Research Site in Falmouth, Massachusetts, are to learn more about the distribution, abundance, population characteristics, grazing efficiency, transport behavior, and role in subsurface contaminant degradation of protozoa in ground water. This paper discusses investigations designed to improve understanding of the subsurface transport of the abundant (up to 10³ /gdw [grams dry weight]) flagellates that inhabit the Cape Cod aquifer. Funding for this work was provided by NSF grant #BCS-9012183 awarded to the University of New Hampshire (UNH). The objective of the experiments discussed herein was to gain information on the degree of retardation, immobilization, and apparent dispersion of the stained flagellates under in situ conditions. A second objective was to compare flagellate transport with that observed for indigenous bacteria in earlier experiments at the Cape Cod site (Harvey and others, 1989; Harvey and Garabedian, 1991) and with particulate tracers (protozoa-sized microspheres) in the laboratory (Harvey and others, 1993).

METHODS

The test involved an unconfined, sandy, outwash aquifer that has been contaminated by a 4.5 km-long plume resulting from on-land disposal of treated sewage (fig. 1). Flagellates were isolated from aquifer sediments sampled from a depth of 8.5-10.1 m in the contaminated zone near the tracer-test site. The flagellates were grown in nutrient media (Page, 1988) and labeled with the vital stain, hydroethidine (Harvey and others, 1993). Ground water (100 L) containing labeled flagellates (2.2 x 10⁷/L) and bromide (165 mg/L) was added slowly to the aquifer, by use of a peristaltic pump, at depths of 9.0 and 9.3 m at
USGS well M4-15 (fig. 1). The injection well is within a large (20 by 220 m) array of 15-port multi-level samplers (MLS) (LeBlanc and others, 1991) and within 100 m of where several in situ experiments were conducted to assess the subsurface transport of microbial-sized microspheres and indigenous bacteria (Harvey and others, 1989; Harvey and Garabedian, 1991; Harvey and others, 1993). Ground-water samples (500 mL) were collected daily at wells M4-15A and M5-15 in order to capture breakthrough of both bromide and stained-flagellates 1 and 2 m down-gradient from the point of injection.
Bromide was analyzed using a specific-ion electrode and labeled flagellates were enumerated by epifluorescence microscopy. Samples of ground water (50-250 mL) were fixed (1 % final concentration) with glutaraldehyde that had been buffered in 0.001 M cacodylate (pH 7) and filtered onto 25 mm-(diameter), 0.8-μm pore size, black polycarbonate filters. Enumerations of hydroethidine-labeled flagellates were made under incident ultraviolet light by use of an epifluorescence microscope that was fitted with a 400 nm dichroic mirror, 330 to 380 nm excitation filter, and 420 nm barrier filter.

RESULTS

Results of the field transport experiment are given in figures 2 and 3, which depict the dimensionless concentration histories (breakthrough curves) of labeled protozoa and bromide at wells M4-15A and M5-15 (about 1 and 2 m downgradient from the point of injection). At 1 m downgradient (figure 2), the peak bromide concentration was approximately the same as that present in the injectate (that is, \( \frac{C}{C_0} = 1.0 \)), which suggests that well M4-15A lies squarely along the trajectory of the injectate cloud. The breakthrough curve for bromide was characterized by a single peak, which occurred approximately 2 days after injection. Relative to bromide, the center of mass for the stained flagellates was retarded by longer than 1 week. Also, the breakthrough curve for the protozoa had two distinct peaks of approximately equal magnitude and an elongated tail. The initial peak arrived at well M4-15A 1 day earlier than the bromide peak. The second peak arrived 3 days after the bromide peak.

At 2 m downgradient (figure 3) from the point of injection, peak bromide concentration was less than 30 percent of that present in the injectate as a result of dispersion and a downgradient sampling coordinate that may have been slightly off center with respect to the trajectory of the center of bromide mass. The peak in bromide concentration appeared to pass well M5-15 about four days after injection. Again, the breakthrough curve for the stained protozoa was characterized by multiple peaks with a center of mass that was substantively retarded (at least 1 week) relative to bromide. Although bromide concentrations returned to background levels at well M5-15 approximately 12 days after injection, substantive numbers (more than \( 4 \times 10^4 /L \)) of stained-protozoa were still observed 45 days into the test.

DISCUSSION

Substantial retardation factors (RF = 2-3) for ground-water flagellates has been observed in flow-through columns packed with sieved (0.5 to 1.0 mm grain size) aquifer sediments (Harvey and others, in
In contrast, peak breakthrough of stained, indigenous bacteria in previous forced- and natural-gradient tracer tests occurred coincidentally with or slightly before the bromide peak (Harvey and others, 1989; Harvey and Garabedian, 1991). However, substantial retardation has been observed for various types of microspheres and has been found to increase with the reactivity of their surfaces (Harvey and others, 1989). Retardation of colloids in the Cape Cod aquifer is also affected by physical heterogeneity (Harvey and others, 1993).

The rate of flagellate immobilization (almost 100 fold per meter of travel distance) is several orders of magnitude greater than that observed for the indigenous bacteria traveling through these same sediments (Harvey and Garabedian, 1991). However, it does not appear that straining (physical entrapment within pores that are smaller than the limiting dimension of the suspended particle) plays a very significant role in the immobilization of the flagellates, judging from grain-size distribution of aquifer sediments in the area of the tracer test (Barber, 1990) and the prerequisite ratio of cell diameter to critical pore size of 1.5 (see, for example, Matthess and Pekdeger, 1985). Optimal size for transport of spherical colloids with buoyant densities of 1.05 appears to be approximately 2 μm, judging from predictions made with a physical model and the results of column experiments involving 0.45 to 4.8 μm microspheres (Harvey and others, 1993). It is more likely that most of the immobilization is caused by sorption, although sorption of ground-water flagellates in the presence of aquifer mineral surfaces has not been investigated.

The comparatively large apparent dispersion exhibited by the flagellates relative to that of bromide suggests that the chemical (diffusive) and hydrodynamic components of dispersion do not adequately describe the spreading of the protozoan peak at either well M4-15A or M5-15. A large disparity between the apparent dispersion of the conservative tracer and of the microbes was not observed for bacteria. However, large degrees of apparent dispersion were observed in earlier tracer experiments involving highly reactive carboxylated microspheres (Harvey and others, 1989; Harvey and others, in press). The role of motility in the apparent dispersion of the stained flagellates is not known and was beyond the scope of our experiment. However, substantive transport was observed only in the direction of flow and where there was significant breakthrough of bromide.

CONCLUSION

The cultured ground-water flagellates used in this experiment appear to be immobilized very quickly in the presence of aquifer sediment grain surfaces, even though the small (approximately 2 μm) flagellates may be near the optimal size for advective transport in this habitat. The tendency of the flagellates to become immobilized at grain surfaces likely results in transport characteristics that are significantly different than those observed for the indigenous bacteria that may serve as a food source. Relative to the bacteria, the flagellates are subject to substantial retardation and apparent dispersion during downgradient transport through aquifer sediments. Additional research is needed on the role of motility and encystment in the mobility of protozoa in contaminated aquifers.

ACKNOWLEDGMENT

We thank John Loveland (University of Colorado) and others for reviews of the manuscript.

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Use of Static Column Experiments to Identify Factors Affecting Bacterial Attachment in Contaminated Aquifer Sediments From Cape Cod, Massachusetts

By David W. Metge¹, Ronald W. Harvey¹, George R. Aiken¹, and Larry B. Barber, II¹

Abstract

The mineralogy of sediment in, and geochemistry of, ground water from the Cape Cod contaminated aquifer have been found to affect bacterial attachment and transport through aquifer sediments. Static column experiments, under simulated aquifer conditions, were used to identify chemical factors (for example, pH, the concentration of dissolved organic carbon [DOC], the presence and concentration of divalent ions and other competing ligands, and ionic strength) which can affect bacterial transport in the subsurface. pH strongly affected bacterial attachment in uncontaminated sediments; an increase in pH from 5.8 to 7.9 resulted in a 70 percent drop in fractional bacterial attachment. Also, attachment of bacteria to aquifer sediments was substantially affected by changes in the amount and type of DOC from both contaminated and uncontaminated ground water. Finally, ionic strength and divalent ions, such as sulfate, were found to affect bacterial attachment. The experiments indicate that competitive and (or) synergistic interactions can operate under different pH conditions. Thus, different geochemical conditions can affect cell-grain surface interactions by competing with bacteria for binding sites and (or) by modifying grain or cell-surface characteristics.

INTRODUCTION

Bacterial transport through contaminated ground water is receiving increasing focus, because bioremediation is often advocated as a solution to contamination problems. Introduction of genetically engineered or contaminant-adapted bacteria to contaminated aquifers can be a more suitable approach than engineering approaches, such as "pump-and-treat," which might not be effective in handling low levels of ground-water contamination. Bacterial-transport studies (Harvey and others, 1989; Scholl and Harvey, 1992) have shown that bacterial attachment and the extent of transport can be affected by a number of complex physical and chemical factors, the most important of which are pH, ground-water chemistry, the amount of sediment-associated organic and metal-oxide material, and sediment mineralogy.

Static column experiments, designed to simulate aquifer conditions, were performed to determine the effect of specific chemical factors on bacterial attachment and transport characteristics. The goal of these experiments was to determine how bacterial attachment in contaminated and uncontaminated ground water (over a pH range of 3-9) was affected by (1) the amount and type of DOC; (2) ionic strength; and (3) sulfate (SO₄²⁻) concentrations. Results presented here show how differences in ground-water geochemistry affect bacterial attachment to aquifer sediments, and how contributions of geochemical constituents are affected by pH.

MATERIALS AND METHODS

Site Description and Sample Collection

Samples were collected from the Cape Cod Toxic-Substances Hydrology Research site. The study site is a sand and gravel aquifer located on Cape Cod, Mass. Disposal of secondary-treated sewage in infiltration beds since 1936 has resulted in an extensive plume of contaminated ground water.
Figure 1. Location of sampling sites, Cape Cod Toxic-Substances Hydrology Research site, Cape Cod, Mass. (modified from LeBlanc, 1984).
Contaminated ground water (CGW) was collected from a well (S314-51) located in the core of the plume and about 30 m downgradient from the sewage outfall. Water samples from this well were collected at a depth of 15.5 m (about 6.4 m below the water table). Uncontaminated ground water (UGW) and sediments were collected from well F350-13, 3 km downgradient from the sewage infiltration beds at a depth of 3.9 m (about 2.7 m below the water table). This depth is well above the plume of contaminated ground water. Sediment samples were collected with a piston-type core barrel using a hollow-stem auger (Zapico and others, 1987). Locations of sampling sites are shown in figure 1. Samples were maintained at 4° C until processed. Ground-water chemistries were analyzed according to published methods (Brinton and others, written communication; Garbarino and Taylor, 1979). Summaries of these chemical data are provided in table 1.

**Table 1. Summary of chemistry data for contaminated and uncontaminated ground water from Cape Cod Toxic-Substances Hydrology Study Site**

<table>
<thead>
<tr>
<th>Chemical property</th>
<th>Uncontaminated ground water</th>
<th>Contaminated ground water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na+ concentration (1)</td>
<td>8.4 mg/L</td>
<td>47.3 mg/L</td>
</tr>
<tr>
<td>Cl- concentration (2)</td>
<td>11.8 mg/L</td>
<td>12.3 mg/L</td>
</tr>
<tr>
<td>SO4-2 concentration (2)</td>
<td>7.1 mg/L</td>
<td>28.2 mg/L</td>
</tr>
<tr>
<td>DOC concentration (3)</td>
<td>0.9 mg/L</td>
<td>3.9 mg/L</td>
</tr>
<tr>
<td>Specific Conductance</td>
<td>62 µS/cm</td>
<td>488 µS/cm</td>
</tr>
<tr>
<td>Ionic Strength (1) (4)</td>
<td>0.8 x 10⁻³</td>
<td>4.5 x 10⁻³</td>
</tr>
<tr>
<td>pH</td>
<td>4.9</td>
<td>5.9</td>
</tr>
</tbody>
</table>

(1) Ionic species measured with inductively-coupled atomic-emission spectroscopy.
(2) Ionic species measured by ion chromatography.
(3) DOC concentration measured by carbon analysis.
(4) Calculated from totals of ionic species.

**Experimental Procedures**

Static column experiments were performed by the method of Scholl and Harvey (1991, 1992). The method simulates aquifer conditions but avoids applicability problems inherent with stirred-batch systems; all bacteria used in the experiments were indigenous bacterial populations from CGW. The following modifications were made. Fifteen grams of sieved sediment (0.5-1.0 mm grain size) were used in all experiments. The number of bacteria loaded into each column was kept constant (70 x 10⁶ cells/mL, 4.7 x 10⁶ cells/g sediment) in all experiments. These were significantly greater than what was used previously (20-40 x 10⁶ cells/mL, 1-4 x 10⁶ cells/g sediment). These modifications facilitated comparison between experimental treatments and improved resolution of the effects of geochemical conditions. All experiments were performed in a refrigerated incubator (10° ± 1° C).

Ground waters from an uncontaminated well and from a well within the contaminant plume were used to examine how contaminant concentrations in the plume affect bacterial attachment to aquifer sediments. Untreated, uncontaminated and untreated, contaminated ground waters were used (over a range in pH of 3-9) in static column experiments to assess bacterial attachment in contaminated and uncontaminated parts of the aquifer.

Static-column experiments were performed with two types of treated water to examine how the concentration and type of DOC present in untreated CGW affect bacterial attachment to aquifer sediments. For the first experiment, contaminated ground water, adjusted to pH 7.0, was passed through a column packed with XAD-8, a nonionic macroporous resin, to remove the hydrophobic neutral fraction of DOC from CGW (Aiken and others, 1992). Water for the second experiment was prepared by ultraviolet (UV)-oxidation of DOC in CGW using a quartz flow-through cell containing an 185 nm UV light source. Contaminated ground water (1.2 L) was recirculated through the UV unit for 16 hours (~10° C) with a peristaltic pump operating at approximately 4 mL/min. All DOC concentrations were determined by carbon analyzer.

The degree of fractional bacterial attachment to sediments was examined by changing ionic strength, DOC, and SO₄²⁻ in CGW and UGW. The effect of ionic strength on bacterial attachment in the presence and absence of naturally occurring DOC was examined by using two treatments to UGW. For the first experiment, specific conductance was increased in UGW by NaCl amendment to approximate specific conductance levels in CGW (488 µS/cm). For the second experiment, UV-oxidized UGW was amended with NaCl for comparative purposes. We examined elevated concentrations of sulfate in contaminated and uncontaminated ground water to determine the effect of sulfate on bacterial attachment.
RESULTS AND DISCUSSION

Overall Effects of Contaminants on Bacterial Attachment

Attachment experiments were performed with indigenous bacterial populations from CGW, using untreated UGW or CGW (over a pH range of 3-9), and sediments from an uncontaminated area of the aquifer. The pH strongly affected fractional bacterial attachment in the presence of untreated UGW. A 70 percent drop (from 92 to 21 percent) accompanied a 2-unit increase in pH (pH 5.8 to 7.9). This increase in attachment under acidic pH conditions may be analogous to observations of increased sorption of dissolved organic materials to oxide surfaces with a decrease in pH (Davis, 1982). The effects of pH on bacterial attachment to sediments in untreated CGW was less clear. Fractional bacterial attachment varied by only 16 percent (from 67.4 to 83.7 percent) over the pH range of 3.5 to 8.8. Substantially greater attachment occurred under slightly acidic to alkaline conditions (pH 6.5-8.0) and less attachment occurred under acidic conditions than in untreated UGW over the same pH range. These observations corroborate results seen with similar aquifer material and conditions (Scholl and Harvey, 1992). The results indicate that DOC or the inorganic chemical matrix within CGW suppresses bacterial attachment under acidic to mildly acidic conditions, but promotes attachment under neutral to alkaline conditions.

Effects of DOC On Bacterial Attachment

The degree of fractional bacterial attachment to aquifer sediments was affected by slight changes in concentration and type of DOC present in CGW. When compared to the degree of bacterial attachment observed for untreated CGW over the pH range of 3.5-6.0, removal of the hydrophobic-neutral fraction of DOC (about 3 percent of the total DOC) from CGW by passage through a nonionic macroporous ion exchange resin (at pH 7.0) increased bacterial attachment under acidic to mildly acidic conditions. However, the same relative fractional attachment as untreated CGW was observed at pH 6.1, indicating that the hydrophobic neutral fraction of CGW may suppress attachment under acidic pH conditions. When virtually all DOC from CGW was removed by UV oxidation (97 percent of DOC removed), a 20 to 45 percent decrease in fractional bacterial attachment above pH 5.5 resulted, indicating that DOC other than the hydrophobic neutral fraction of DOC in CGW promoted bacterial attachment under alkaline conditions. It is not clear whether the DOC alters grain surfaces and (or) changes bacterial-surface sites. Other studies on adsorption of DOC to grain surfaces have indicated that DOC masks positive surface charges associated with iron oxyhydroxide coatings on grain surfaces (Davis, 1982). Results from our experiments indicate that, if masking of mineral surface charge by DOC occurs, the mechanism can promote or suppress attachment under differing pH conditions.

Effects of DOC / Ionic Strength on Bacterial Attachment

The pattern of bacterial attachment in ionic-strength-adjusted UGW was substantially different in the presence and absence of naturally occurring DOC. The specific conductance of UGW was raised 8-fold (from 62 to 480 μS/cm) and ionic strength was doubled (from 8 x 10^-4 to 1.6 x 10^-3) by addition of NaCl to UGW. Bacterial attachment to sediments in ionic-strength-adjusted UGW in the presence of DOC was increased (over the pH range 6-9) when compared to levels of bacterial attachment in untreated CGW. However, ionic strength adjustments to UGW (UV-oxidized) in the near-absence of naturally occurring DOC had less of an effect on bacterial attachment compared to levels observed in UGW that was only altered with respect to ionic strength. This indicates that naturally occurring and anthropogenically derived DOC can affect bacterial attachment in different ways.

Effect of Sulfate on Bacterial Attachment

Elevated concentrations of $SO_4^{2-}$ can also play a significant role in bacterial attachment to aquifer
sediments. The effect of elevated SO$_4^{2-}$ concentrations was assessed by amending UGW (7.1 mg/L SO$_4^{2-}$) with Na$_2$SO$_4$ to concentrations comparable to those in CGW (28 mg/L SO$_4^{2-}$). A second system was prepared by destroying DOC in CGW by UV oxidation for 16 hours. This was done because the effects of SO$_4^{2-}$ in CGW could be masked by levels of DOC present in untreated CGW. Sulfate amendment to UGW decreased fractional bacterial attachment to aquifer sediments in the range of pH 4.5-6 relative to the extent of bacterial attachment seen with unamended UGW. DOC removal from CGW decreased bacterial attachment to levels similar to those of sulfate-amended UGW, suggesting that SO$_4^{2-}$ might compete with bacteria for sediment-grain binding sites and (or) alter cell-surface characteristics.

SUMMARY

We found that low (part-per-million) concentrations of DOC and SO$_4^{2-}$ concentrations and modest (several-fold) changes in ionic strength can affect bacterial attachment to aquifer sediments. However, pH appears to be the primary factor governing bacterial attachment and transport. Competitive, synergistic, and inhibitory mechanisms appear to be affected by pH. More experiments are planned with natural and human-derived DOC (for example, humic acids and analogs of contaminant ionic and nonionic surfactants) to define the mechanisms governing bacterial attachment to aquifer sediments in the presence and absence of organic material. Also, the influence of divalent cations, such as Mg$^{2+}$, Ca$^{2+}$, and anions, such as SO$_4^{2-}$, and their interaction with DOC to affect bacterial attachment deserve closer examination. These experiments were done with indigenous bacterial communities that are a heterogeneous mix of populations, each with different cell-surface characteristics that can differ in how they are affected by the plume geochemistry. Ultimately, we will apply results from the static-column experiments to field tracer tests to determine how contaminants affect bacterial transport.

REFERENCES


An Experiment to Quantify Temporal Variability of Water Samples Obtained from Screened Wells, Cape Cod, Massachusetts

By Thomas E. Reilly\textsuperscript{1} and Denis R. LeBlanc\textsuperscript{2}

Abstract

The chemical composition of water sampled from some screened wells has been observed to exhibit sustained temporal variability. Results from a field experiment, undertaken on August 12, 1992, in the area of the contaminant plume from the Otis Air Base sewage-disposal sand beds, support the recent hypothesis that the temporal variability can be attributed to the flux along the well screen reflecting the spatial heterogeneity in hydraulic conductivity and water chemistry of the aquifer near the well. The experiment consisted of withdrawing water from a well with a screened interval approximately 40 ft long and sampling over time during a 5-hour period. Water samples also were collected from multilevel samplers surrounding the well before, during, and after the pumping of the well. Selected constituent concentrations and properties measured in samples collected from the discharging well showed different temporal trends during the 5-hour test. For example, the ferrous iron concentration decreased, the calcium concentration increased, and specific conductance remained relatively constant. The different trends are due to the different distributions of the constituents around the well as documented by analysis of water samples collected by the set of multilevel samplers. The observed trends are in agreement with the hypothesis and apparently are due not to the purging of the water standing in the well but to the flow and transport of the water and chemical species in the heterogeneous aquifer in the immediate vicinity of the well.

INTRODUCTION

Water that enters a well through a well screen is derived from different layers of porous material. These layers are present at different scales and can be characterized by different physical properties, such as hydraulic conductivity, and chemical properties. Layer boundaries defined by one property may not coincide with those defined by a different property. The water withdrawn from the well is a composite of the waters present in these different layers along the length of the screen. The length of well screens can span vertical distances of as little as 1 foot or as much as 100 or more feet. The rate of water withdrawn from each layer is variable and depends on the hydraulic conductivity, screen placement, pump-intake placement, and other factors.

Wilson and Rouse (1983), Rivett and others (1990), Gibs and Imbrigiotta (1990), Reilly and Gibs (1993), and others have observed that chemical concentrations of various constituents can change in the water discharging from a well over the time of sampling. Thus, questions arise as to what the concentration of the constituent is in the ground water, or what water is actually being sampled. Some of the observed temporal changes are due to the removal of water that had been residing in the well casing prior to sampling; but some of this variation appears to persist. The persistent temporal variations in the concentrations may be due to both the chemical and hydraulic-conductivity distributions in that part of the aquifer that contributes water to the well.

The variability of hydraulic conductivity in ground-water systems is widely recognized. Wolf and others (1991) and Hess and others (1992) recently showed considerable variation in hydraulic conductivity, on the scale of centimeters, in the sand and gravel aquifer at Cape Cod, Mass. Geochemical investigations, also conducted on Cape Cod, Mass. (Smith and others, 1991), indicated the necessity of collecting closely spaced samples for chemical measurements because of the vertical variability in chemistry over small distances.
The purpose of this paper is to describe an experiment performed at Cape Cod, Mass., to examine the hypotheses that (1) the observed concentrations of constituents in the water sampled from a screened well are due to the flux of these constituents into the well as determined by the hydraulic conductivity and chemical distribution near the well, and (2) the changes in concentration observed from samples collected continually from a long screened well can be interpreted to aid in understanding the hydraulic and chemical properties of the aquifer that is the source of water to the well.

DESCRIPTION OF THE EXPERIMENT

The experiment was designed to evaluate the chemistry of the water discharged from a well screened in a physically and chemically heterogeneous aquifer. Well F453-63 was selected because it was known that the screen penetrated both the oxic and anoxic zones of the sewage plume from the Otis Air Base sewage-disposal sand beds (fig. 1). The ground-water chemistry differs in the oxic and anoxic zones, thereby providing a heterogeneous chemical environment along the screened interval of well F453-63. Three multilevel

Figure 1. Ground-water study site on Cape Cod, Massachusetts, showing the location of the contaminant plume and the screened well used in the well-purging experiment.
samplers were installed near well F453-63 to describe the chemical distribution in the immediate vicinity of the screened well (fig. 2). The hydraulic conductivity distribution of the aquifer along the screen in well F453-63 ranges from 77 to 958 ft/d (Kathryn Hess, U.S. Geological Survey, written comm., 1993) as determined by the flowmeter method of Hess and others (1992).

Well F453-63 is constructed of 2-inch inside-diameter polyvinyl chloride (PVC) pipe with four sections of 10-ft-long flush-joint threaded 2-inch inside-diameter PVC screens. The screen extends from an altitude of 4.7 to 43.7 ft above sea level and the initial water-table altitude was 44.33 ft above sea level at the time of the test. The volume of water residing in the casing and screened section of the well is approximately 0.943 ft³. The multilevel samplers installed in the vicinity of well F453-63 had 13 or 14 ports in the saturated zone. Each multilevel sampler consists of 15 color-coded polyethylene tubes (0.25-inch outside diameter). The tubes run from land surface down the inside of a 1.25-inch inside-diameter PVC casing and out holes spaced every 3.3 ft drilled through the PVC. The open, down-hole end of each tube is screened with a fine nylon fabric.

The experiment was undertaken on August 12, 1992. Well F453-63 was sampled over time, and the multilevel samplers were used to document the chemical distribution in the ground water in the immediate vicinity of the well. A variable rate submersible pump was set 0.5 ft below the static water level in well F453-63. The continuous discharge from the screened well was measured 15 times during the 5-hour experiment using a graduated cylinder; discharge ranged from 0.047 to 0.051 ft³/min, indicating that a volume equivalent to one casing volume is discharged about every 20 minutes. Water-level measurements were made before pumping, just prior to the end of the test, and a half hour after the end of the test. Drawdown was measured to be 0.02 ft in the pumped well after 5 hours of pumping.
The long-screen well was pumped for 5 hours and sampled at 5 minutes after discharge began, then every 10 minutes for the first 2 hours, and finally every 15 minutes for the remaining 3 hours. Water samples were collected from the three multilevel samplers before and after the test to observe any changes in constituent concentration in the immediate vicinity of the well screen. Multilevel sampler 2 was also sampled halfway through the experiment. All water samples were analyzed in the field for specific conductance, pH and ferrous iron (Fe\(^{2+}\)) concentration. The samples were subsequently analyzed for concentrations of boron, calcium, chloride, iron (Fe total), phosphorous, potassium, magnesium, manganese, sodium, zinc, and nitrogen species, including nitrous oxide, ammonium, nitrite and nitrate.

**DATA FROM EXPERIMENT FOR SELECTED CONSTITUENTS**

The distribution with depth of specific conductance, and concentrations of ferrous iron, calcium, chloride, and nitrous oxide (N\(_2\)O) from multilevel sampler 2 during the test is shown in figure 3. The vertical distributions of the specific conductance and the chemical constituents are all different. The vertical variability in concentration is significant and concentrations change over short vertical distances. This vertical variability is expected because of the presence of the sewage plume, which is intersected by the screen of well F453-63. The specific conductance and four chemical constituents were chosen for collection because of their expected different distributions along the well screen.

**Figure 3.** Concentration distribution with depth of specific conductance, ferrous iron, calcium, chloride, and nitrous oxide at multilevel sampler 2 after approximately 2.5 hours into the test.
Almost identical specific conductance and concentration distributions were found in all three multilevel samplers, indicating that the specific conductance and constituent concentrations are relatively uniform laterally (at least on the scale of feet) although they are very variable vertically.

The water discharging from the screened well was collected and analyzed as described above. The specific conductance and concentrations of ferrous iron, calcium, chloride, and nitrous oxide as measured during the course of the experiment are shown in figure 4. The concentrations of these selected constituents over time show some variability; for example, ferrous iron decreased, calcium increased, and chloride remained relatively constant.

**IMPLICATIONS OF THE EXPERIMENTAL DATA ON WELL-PURGING CRITERIA**

Reilly and Gibs (1993) simulated a hypothetical system to illustrate that the composition of water discharging over time from a physically and chemically heterogeneous aquifer can change over time depending on the distribution of the chemical constituents of the water and the hydraulic conductivity of the aquifer. They showed that changes over time are not necessarily due to the evacuation of the stagnant water in the well casing, but can also be due to the transport of the chemical constituents through the aquifer to the well. The results to date at the Cape Cod well-purging experiment corroborate these simulations.

![Figure 4](image-url)
When a constituent or property has little variation over the screened interval, such as for the specific conductance and chloride concentration at well F453-63, the concentration or value of the property in the water discharging from the well changes little or not at all over time once the standing water in the well is removed. However, when the chemical distribution is variable along the screened interval, as was the case for ferrous iron, calcium and nitrous oxide, the concentration of the constituent in the water discharging from the well does not necessarily remain constant as the well is pumped. The concentration of ferrous iron in the ground water in the screened interval of the well remained near or below the detection limit from the water table to about half way down the screened interval and then rapidly increased to about 20 mg/L for the bottom half of the screened interval (fig. 3). The corresponding temporal trend in the concentration of ferrous iron in the water pumped from the screened well continuously decreased from about 8 to 6 mg/L during the 5-hour test. In contrast, the concentration of calcium in the ground water in the screened interval of the well decreased from about 15 mg/L over the top half of the screen to about 5 mg/L over the bottom half of the screened interval (fig. 3). The concentration of calcium continuously increased over time from about 7 to 9 mg/L during the 5-hour test (fig. 4). The nitrous oxide concentration in the ground water has a peak concentration of 20 μM in the middle of the screened interval (fig. 3). The trend of the nitrous oxide concentration from the pumped well over the 5-hour test is unclear (fig. 4).

It is important to note that a volume of water equal to the amount of water stored in the well is discharged approximately every 20 minutes. The observed temporal trends for the ferrous iron and the calcium concentration are persistent over the 5-hour test, during which time approximately 15 casing volumes were evacuated. The mixing of the water in the well bore will also affect the temporal distribution of concentration to a degree, but the persistence of the observed trends and the hypothetical numerical experiments of Reilly and Gibs (1993) indicate that the primary cause of these trends is a result of flow and transport within the heterogeneous aquifer system. Thus, the observed trends in water chemistry over time are not due to the purging of the water standing in the well but rather are due to the flow and transport of the water and chemical species in the aquifer in the immediate vicinity of the well.

The data obtained from multilevel samplers 1, 2 and 3 indicate that the water chemistry was relatively constant laterally around the well in each layer, even though the vertical variation in water chemistry between layers can be great. The amount of water discharged from the screened well over the entire 5-hour test period was approximately 14.4 ft³. This volume of water would be removed from a cylinder of aquifer material (assuming a porosity of 0.4) that extends about 0.5 ft away from the well screen. The water at the multilevel samplers did not move much and is representative of the temporal and areal variation in water chemistry around the well. Thus, the temporal trends observed in the water discharging from the pumped well are probably due primarily to the vertical variations in water chemistry and the hydraulic conductivity of the aquifer. Flowlines will converge on the layers of high hydraulic conductivity and transport solutes vertically into different layers as the well is pumped. This mixing of waters of differing composition can cause the water chemistry in the water mixture in the discharging well to change over time until a steady transport field is developed.

FUTURE STUDY PLANS

Work is currently progressing on the numerical simulation of the experiment. The simulation of the transport processes in the screened zone will attempt to reproduce quantitatively the observed temporal concentration trends in the discharge water from the screened well. The solute-transport simulation of the ground-water system, which will use cylindrical coordinates, will incorporate the estimated hydraulic conductivity distribution and the chemical distribution determined in this experiment. This simulation will enable the mass of the differently distributed chemical species entering the well screen to be estimated quantitatively. The additional process of transport within the well bore itself also will be evaluated. This simulation can either corroborate or prove invalid the hypothesis that the observed trends are indeed due to the physical and chemical heterogeneity in the aquifer.

SUMMARY

The chemical composition of water pumped from some screened wells has been observed to exhibit sustained temporal variability. Results from a field
experiment, in the area of a contaminant plume from the Otis Air Base sewage-disposal sand beds, support a recent hypothesis that such temporal variability can be attributed to the flux along the well screen reflecting the spatial heterogeneity in hydraulic conductivity and water chemistry of the aquifer near the well. The experiment consisted of withdrawing water from a well with a screened interval approximately 40 ft long and sampling over time during a 5-hour period. Water samples also were collected from multilevel samplers surrounding the well before, during, and after the pumping of the well. All water samples were analyzed in the field for specific conductance, pH and ferrous iron. The samples were subsequently analyzed for boron, calcium, chloride, iron (Fe total), phosphorus, potassium, magnesium, manganese, sodium, zinc, and nitrogen species, including nitrous oxide, ammonium, nitrite, and nitrate.

The data collected from this experiment show that the chemical composition of water discharging from a screened well in a physically and chemically heterogeneous aquifer can have persistent variations over time. The concentrations of selected constituents in the water sampled over time from the discharging well show trends that appear to be associated with the vertical distribution of these constituents in the aquifer. The chemical data collected during the experiment corroborates results of earlier work that indicate that these trends depend on the distribution of the chemical constituents and the hydraulic conductivity around the well.

REFERENCES


Preliminary Type-Curve Analysis of an Aquifer Test in an Unconfined Sand and Gravel Aquifer, Cape Cod, Massachusetts

By Allan F. Moench¹, Denis R. LeBlanc², and Stephen P. Garabedian²

Abstract

An aquifer test was conducted in a sand and gravel, glacial-outwash deposit on Cape Cod, Massachusetts. A partially penetrating well was pumped at a constant rate of 320 gallons per minute for 72 hours. Changes in hydraulic head were observed at 20 locations through observation wells and piezometers distributed both radially and vertically within the saturated zone of the aquifer. The test was analyzed using Neuman's analytical model for flow to a partially penetrating well in a water-table aquifer. On the basis of geophysical well logs, cores, and other investigations conducted in the local area, the aquifer was initially assumed to have a saturated thickness of 80 feet for the purpose of analysis. However, drawdown observed in a piezometer located 108 feet below the water table, and an initial analysis, revealed a complete lack of conformity between theoretical and observed drawdown in piezometers located near the pumped well. Also, the computed horizontal hydraulic conductivity was twice that obtained by independent studies. Ongoing studies of the regional stratigraphy indicate that the saturated thickness of the aquifer is actually closer to 160 feet than to 80 feet. By increasing the assumed saturated thickness to 160 feet, the theoretical drawdown was found to match observed drawdown for most of the test period at nearly all points of observation. Results indicate that there is a remarkable degree of aquifer homogeneity with respect to flow at the scale of the test. The aquifer transmissivity and specific yield were determined to be 38 feet squared per minute and 0.23, respectively, and the ratio of vertical to horizontal hydraulic conductivity was estimated to be about 1:2.

INTRODUCTION

As part of an effort to quantify the hydraulic properties of the unconfined, sand and gravel, glacial-outwash aquifer at the Cape Cod Toxic-Substances Hydrology Research site near Falmouth, Massachusetts, a 72-hour aquifer test was carried out in August, 1990. The test was run by pumping a well at a constant rate and by observing the resulting changes in hydraulic head at locations that differ in distance and azimuth from the pumped well and in depth below the water table. In this paper transmissivity, horizontal and vertical hydraulic conductivity, and specific yield are estimated by type-curve analysis using the Neuman (1974) analytical model for flow to a partially penetrating well in a water-table aquifer.

WELL-AQUIFER CONFIGURATION AND DATA COLLECTION

Although the unconsolidated sediments in the test area are approximately 300 ft thick (LeBlanc, 1984), studies indicate that clean, medium to coarse-grained, high-permeability glacial outwash overlies fine-grained, relatively low-permeability material at a depth of about 80 ft below the water table (Hess and others, 1992). The pumped well (well F507-080),
which was installed in July 1990 for this aquifer test and a concurrent forced-gradient tracer test, was drilled by cable-tool methods to a depth of about 80 ft below land surface. Located within an abandoned gravel pit, the well is 33 ft south and 76 ft west of the origin of coordinates (well no. F343-036 in figure 1) on a magnetic-north oriented grid (LeBlanc and others, 1991). An 8-inch inside-diameter (i.d) polyvinyl chloride (PVC) casing was installed with an 8-inch i.d PVC screen along the bottom 47 ft of the well. Backfill consisted only of natural collapse material and cuttings from the hole. The top and bottom of the screen were located 13.2 and 60 ft, respectively, below the initial water table, which was approximately 19 ft below land surface. Observation piezometers and wells were constructed by auguring to prescribed depths and installing 2-inch i.d. PVC casings with 2-ft-, 9-ft-, or 39-ft-long PVC screens. Changes in hydraulic head were observed at 20 locations (see table I and figure 1) and at the pumped well.

In August 1990, well F507-080 was pumped at a rate of 320 gal/min for 72 hours. Discharge water was diverted through fire hose to the Otis Air Base sewage-infiltration beds located about 500 to 600 ft upgradient (north) of the test area. The rate of well discharge was monitored by a manometer and orifice at the discharge point and by noting the time required to fill a 55-gal drum at the end of the fire hose. Adjustments to the wellhead valve were made as necessary to maintain a constant flow rate. Water levels in piezometers and observation wells analyzed in this paper were measured manually using a steel tape. In addition, pressure transducers were used at 12 of the locations. Drawdown in the pumped well was monitored with an electric tape. Just prior to the end of the test the drawdown in the pumped well was 4.2 ft.

RESULTS AND ANALYSIS

This analysis was performed using the analytical model of Neuman (1974) for flow to a partially penetrating well in a water-table aquifer. Model parameters are defined in table 2. Only manual measurements of hydraulic head are used in the analysis as very early measurements are not needed. To perform the analysis, head measurements were converted to drawdown, and time was divided by the square of the radial distance between the pumped well and the point of observation. Composite time-drawdown plots (h as a function of \(t/r^2\)) were then drawn for type-curve analysis. The procedure described by Moench (1993) was used to generate computed values for the type curves. Assuming an initial saturated thickness of 80 ft, close agreement was obtained between theoretical type curves and drawdown observed at distant locations, but drawdown at locations close to the pumped well bore no resemblance to the theoretical type curves. The transmissivity and specific yield obtained from the analysis were 40 ft²/min and 0.14, respectively. The ratio of vertical to horizontal hydraulic conductivity, \(K_v/K_h\), was determined to be 1:5. The horizontal hydraulic conductivity based on the assumed saturated thickness of 80 ft was 0.50 ft/min. This is about twice that obtained in prior studies (Hess and others, 1992). The value of the ratio \(K_v/K_h\) was also less than that obtained by other investigators (Hess and others, 1992).

Observations made during this aquifer test indicate that the change in lithology at a depth of 80 ft is not sufficiently sharp to justify the assumption of an impermeable base to the aquifer at that depth. A plot of drawdown measured in two piezometers located about 14 ft from one another in the horizontal direction and about 90 ft from the pumped well is shown in figure 2. One piezometer is situated about 20 ft above and the other about 26 ft below the hypothesized base of the glacial outwash. Drawdown in both piezometers occurs in direct response to pumping at well F507-080. Thus, a saturated thickness of 80 ft was deemed inappropriate for this analysis.

Because of (1) the lack of agreement between the drawdown at observation points near the pumped well and the theoretical type curves; (2) the presence of drawdown in an observation piezometer 28 ft below the assumed base of the aquifer; and (3) the fact that the calculated hydraulic properties are not in complete accord with those from prior studies, an additional analysis was performed under the assumption that the initial saturated thickness was 160 ft. This value for saturated thickness correlates with a significant change in lithology from coarse to very fine sands based on work cited by LeBlanc (1984, fig. 5) and recent regional geologic studies by John Masterson (USGS, oral commun., 1993). Results of the analysis follow.

Composite time-drawdown plots for the piezometers and observation wells indicated in table 1 are shown in figures 3 and 4. Superimposed on the data are the type curves that resulted in the "best" fit to the data, as determined by visual
Figure 1. Plan view of the positions of the pumped well (F507-080) and observation wells and piezometers in the study area, Cape Cod, Massachusetts.
Table 1. Locations of observation piezometers in study area, Cape Cod, Massachusetts

1Dimensionless ratios are computed assuming a saturated thickness of 160 feet.
2Depth below the initial water table to the top of the screen.
3Data from this well not used in the analysis.

<table>
<thead>
<tr>
<th>Well number</th>
<th>radial distance (ft)</th>
<th>depth(^2) (ft)</th>
<th>screen length (ft)</th>
<th>(z_{D1})</th>
<th>(z_{D2})</th>
<th>(z_D)</th>
<th>((r/b))</th>
</tr>
</thead>
<tbody>
<tr>
<td>F505-032</td>
<td>23.9</td>
<td>10.7</td>
<td>2</td>
<td>0.93</td>
<td>0.022</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F505-059</td>
<td>19.5</td>
<td>30.6</td>
<td>9</td>
<td>0.75</td>
<td>0.81</td>
<td>0.015</td>
<td></td>
</tr>
<tr>
<td>F505-080</td>
<td>21.6</td>
<td>58.4</td>
<td>2</td>
<td>0.63</td>
<td>0.018</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F504-032</td>
<td>46.6</td>
<td>9.6</td>
<td>2</td>
<td>0.93</td>
<td>0.085</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F504-060</td>
<td>49.8</td>
<td>30.0</td>
<td>9</td>
<td>0.76</td>
<td>0.81</td>
<td>0.097</td>
<td></td>
</tr>
<tr>
<td>F504-080</td>
<td>53.1</td>
<td>57.5</td>
<td>2</td>
<td>0.63</td>
<td>0.11</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F383-032</td>
<td>93.0</td>
<td>12.1</td>
<td>2</td>
<td>0.92</td>
<td>0.34</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F383-061</td>
<td>92.9</td>
<td>39.9</td>
<td>2</td>
<td>0.74</td>
<td>0.34</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F383-082</td>
<td>94.8</td>
<td>61.8</td>
<td>2</td>
<td>0.61</td>
<td>0.35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F383-129</td>
<td>96.7</td>
<td>107.8</td>
<td>2</td>
<td>0.32</td>
<td>0.36</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F384-033</td>
<td>137.3</td>
<td>15.8</td>
<td>2</td>
<td>0.90</td>
<td>0.74</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F381-056</td>
<td>159.8</td>
<td>20.0</td>
<td>2</td>
<td>0.87</td>
<td>1.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F347-031</td>
<td>225.7</td>
<td>14.8</td>
<td>2</td>
<td>0.90</td>
<td>1.99</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F434-060</td>
<td>38.6</td>
<td>2.0</td>
<td>39</td>
<td>0.74</td>
<td>0.99</td>
<td>0.058</td>
<td></td>
</tr>
<tr>
<td>F450-061</td>
<td>66.3</td>
<td>1.7</td>
<td>39</td>
<td>0.74</td>
<td>0.99</td>
<td>0.17</td>
<td></td>
</tr>
<tr>
<td>F476-061</td>
<td>65.6</td>
<td>2.2</td>
<td>39</td>
<td>0.74</td>
<td>0.99</td>
<td>0.17</td>
<td></td>
</tr>
<tr>
<td>F478-061</td>
<td>101.3</td>
<td>2.2</td>
<td>39</td>
<td>0.74</td>
<td>0.99</td>
<td>0.40</td>
<td></td>
</tr>
<tr>
<td>3F385-032</td>
<td>224.6</td>
<td>10.0</td>
<td>2</td>
<td>0.93</td>
<td>1.97</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3F377-037</td>
<td>85.1</td>
<td>13.3</td>
<td>2</td>
<td>0.91</td>
<td>0.28</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3F376-037</td>
<td>227.6</td>
<td>13.2</td>
<td>2</td>
<td>0.91</td>
<td>2.02</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The type curves were produced for each piezometer using the dimensionless ratios listed in table 1. The parameters \(D\) and \(d_D\) needed to specify the location of the pumped-well screen, were 0.38 and 0.082, respectively. Given that the saturated thickness is known (or assumed), the only parameter requiring trial-and-error adjustment is the ratio \(K_z/K_P\) which is needed in the model to obtain \(\beta\). A value of \(10^{-2}\) was used for \(\sigma\) in the
Table 2. Dimensionless expressions and notations used in report

<table>
<thead>
<tr>
<th>Expression</th>
<th>Notation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t_{Dy}$</td>
<td>$Tt/r^2S_y$</td>
</tr>
<tr>
<td>$h_D$</td>
<td>$4\pi T(h_i-h)/q_0$</td>
</tr>
<tr>
<td>$\beta$</td>
<td>$K_z r^2/K_r b^2$</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>$S/S_y$</td>
</tr>
<tr>
<td>$d_D$</td>
<td>$d/b$</td>
</tr>
<tr>
<td>$\xi_D$</td>
<td>$\xi/b$</td>
</tr>
<tr>
<td>$z_D$</td>
<td>$z/b$</td>
</tr>
<tr>
<td>$z_{D1}$</td>
<td>$z_1/b$</td>
</tr>
<tr>
<td>$z_{D2}$</td>
<td>$z_2/b$</td>
</tr>
</tbody>
</table>

Notation:
- $b$: initial saturated thickness of aquifer, L
- $d$: vertical distance from initial water table to top of pumped-well screen, L
- $h$: elevation of water table above base of aquifer, L
- $h_i$: initial elevation of water table above base of aquifer, L
- $K_z$: hydraulic conductivity in the vertical direction, $LT^{-1}$
- $K_r$: hydraulic conductivity in the horizontal direction, $LT^{-1}$
- $\xi$: vertical distance from initial water table to bottom of pumped-well screen, L
- $q_0$: pumping rate, $L^3T^{-1}$
- $r$: radial distance from center of pumping well, L
- $S$: storativity
- $S_y$: specific yield
- $T$: transmissivity, $L^2T^{-1}$
- $t$: time since start of pumping, T
- $z$: vertical distance above bottom of aquifer, L
- $z_1$: vertical distance from bottom of aquifer to bottom of observation-well screen, L
- $z_2$: vertical distance from bottom of aquifer to top of observation-well screen, L

computations, but because no attempt was made to evaluate storativity, any value of $\sigma$ less than $10^{-2}$ could have been used. The value of the ratio $K_z/K_r$ that best matches all the drawdown data simultaneously was determined to be approximately 0.5. The "best" overall match point appears to be located at $h_i-h=0.09$ ft and $t/r^2=6 \times 10^{-3}$ min/ft$^2$. On the basis of this match point, the transmissivity is calculated to be 38 ft$^2$/min, the specific yield is 0.23, the horizontal hydraulic conductivity is 0.24 ft/min, and the vertical hydraulic conductivity is 0.12 ft/min.

DISCUSSION

The fact that intermediate-time and late-time drawdown curves fall close to the type curves for a single value of $K_z/K_r$ is an indication that the aquifer is remarkably homogeneous to flow at the scale of this test -- about 20 to 200 feet. The specific yield is about what is expected for clean, well-graded sands. The estimated horizontal hydraulic conductivity is about the same as the geometric mean of values reported by Hess and others (1992), who used a flowmeter to
estimate the vertical distribution of horizontal hydraulic conductivity at 16 wells. The estimated ratio of vertical to horizontal hydraulic conductivity is not inconsistent with the value of 1:1.2 obtained by Hess and others (1992) by statistical methods. The results are also nearly identical to values reported by LeBlanc and others (1988) from an aquifer test conducted about 7,000 ft downgradient. Not all the data are in complete accord with the type curves. The responses in piezometers near the water table generally exhibit greater drawdown at early and intermediate time than expected theoretically. It is possible that these observations can be partially explained by the mechanism of delayed drainage discussed by Nwankwor and others (1992). The overall match point could be fine tuned with additional effort by assuming different values of saturated thickness, but it is unlikely that the final computed hydraulic properties would change substantially. Also, because of the geologic evidence in support of the chosen value of saturated thickness, there would be little justification in altering this parameter in the model.

CONCLUSION

Preliminary analysis of drawdown data collected during a 72-hour aquifer test at the Cape Cod Toxic-Substances Hydrology Research Site was found to yield unambiguous estimates of transmissivity and specific yield. Estimates of vertical and horizontal hydraulic conductivity are consistent with estimates from previous independent studies. The remarkable agreement between observed drawdown and the analytical model indicates not only that the aquifer is reasonably homogeneous to flow but also that the theory adequately describes three-dimensional, axisymmetric flow in clean, well-sorted, glacial-outwash aquifers of the type found at the Cape Cod site.
Figure 3. Composite plot of drawdown data and type curves for a) piezometers F505-032, F505-059, and F505-080 located about 20 feet from the pumped well (F507-080, b) piezometers F504-032, F504-060, and F504-080 located about 50 feet from the pumped well, and c) screened observation wells F434-060, F476-061, and F478-061 located, respectively, 39, 66, and 101 feet from the pumped well, Cape Cod, Massachusetts.
Figure 4. Composite plot of drawdown data and type curves for a) piezometers F383-032, F383-061, F383-082, and F383-129 located about 94 feet from the pumped well (F507-080), and b) piezometers F384-033, F381-056, and F347-031 located, respectively, 137, 160, and 226 feet from the pumped well, Cape Cod, Massachusetts.
REFERENCES


Numerical Simulation of Downward Movement of Solutes During a Natural-Gradient Tracer Test in Sand and Gravel, Cape Cod, Massachusetts

By Denis R. LeBlanc¹ and Michael A. Celia²

Abstract

A numerical, finite-element, solute-transport model was used to test the hypothesis that the downward movement of a tracer cloud observed during a natural-gradient tracer test in sand and gravel on Cape Cod, Mass., was caused, in part, by density-induced sinking. The tracer solution, which included the nonreactive tracer, bromide, was 0.1 percent denser than the ambient ground water. The center of mass of the bromide cloud moved vertically downward about 3.2 meters during 237 days of transport. The model simulated density-dependent flow and solute transport along a two-dimensional vertical section 25 meters high and 136 meters long aligned with the direction of ground-water flow. Transport of the bromide cloud was simulated for a period of 237 days divided into 191 time steps. The temporal pattern of recharge applied to the top boundary of the model was determined from daily precipitation and estimates of evapotranspiration. On the basis of an analysis of spreading of the bromide cloud during the tracer test, dispersivity was increased with time in the simulation asymptotically from 0.05 to 0.96 meters. The simulated downward movement after 237 days was 2.1 meters (about two thirds of the observed movement). The simulation showed that density-induced downward movement was most important during the first 37 days of transport when the density difference between the ambient ground water and the tracer cloud was greatest. Earlier work indicated that the difference between the observed and simulated downward movement may be due, in part, to simulation in only two dimensions of the three-dimensional flow that occurred around the tracer cloud as it moved downward through the ambient ground water. Additional simulations during this and earlier studies showed how the amount of downward movement is affected by the size and shape of the initial bromide cloud; aquifer properties, such as dispersivity and anisotropy of hydraulic conductivity; and the type of boundary used to represent the water table in the model.

INTRODUCTION

A natural-gradient tracer test was conducted in 1985-88 in a sand and gravel aquifer on Cape Cod, Mass. (fig. 1), to measure the dispersion of solutes and relate the dispersion to the spatial variability of hydraulic conductivity (LeBlanc and others, 1991). The test began in July 1985 with the injection of 7.6 cubic meters of tracer solution into the unconfined aquifer. The solution contained a nonreactive tracer, bromide, and two reactive tracers, lithium and molybdate. Movement of the tracers under a natural hydraulic gradient was observed by periodic collection of water samples from a three-dimensional array of 9,840 sampling points.

The location of the center of mass of the bromide cloud was computed for each of 16 sampling rounds by the method of spatial moments (Garabedian

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and others, 1991). The vertical position of the center of mass (one component of the first moment) showed an initial period during which the tracer cloud moved downward. The downward movement during the first 237 days of the test (fig. 2) was 3.2 m (meters), which is about 70 percent of the total downward movement observed during the entire 511-day experiment.

LeBlanc and others (1991) noted that the vertical flow caused by accretion of areal recharge could account for only part of the initial downward movement of the tracer cloud. Ground-water flow is nearly horizontal in the aquifer, and the estimated recharge is insufficient to cause all the observed drop. They hypothesized that the additional downward movement was caused by the density difference between the ambient ground water and the tracer solution. The estimated density of the tracer solution was 1.00037 g/cm³ (grams per cubic centimeter), whereas the estimated density of the ambient, uncontaminated ground water was 0.999409 g/cm³. Although the tracer solution was only about 0.1 percent denser than the ambient ground water, LeBlanc and Celia (1991) used analytical and idealized numerical models to demonstrate that the density contrast may have been sufficient to cause at least part of the observed downward movement. The preliminary modeling also suggested that the amount of downward movement would be affected by the magnitude of the density difference, the dispersivity, and the size of the initial tracer cloud. The purpose of this paper is to describe the use of a numerical model of the field-scale tracer test to test the hypothesis that density caused a significant part of the downward movement observed during the experiment.

**NUMERICAL SIMULATION OF THE TRACER TEST**

SUTRA (Voss, 1984), a two-dimensional finite-element model that simulates solute transport and dispersion in a density-dependent flow field, was used to simulate the first 237 days of the tracer test, when the effect of the density difference on downward movement of solutes was expected to be greatest. The numerical simulation described below used a rectangular grid and assumed that solute concentration and density were linearly related. Also, the dispersivity components were assumed to be independent of the direction of flow (Voss, 1984, p. 48-50).

**Description of Simulation**

The grid was a two-dimensional vertical section encompassing an area 25 m high, the saturated thickness of the sand and gravel (LeBlanc and others, 1991), and 136 m long, the approximate distance traveled by the leading edge of the tracer cloud in 237 days (Garabedian and others, 1991). This area was subdivided into 8,004 rectangular elements arranged in 69 rows and 116 columns. Garabedian and others...
observed that longitudinal dispersivity increased asymptotically during the test to a value of 0.96 m, whereas transverse vertical dispersivity was less than 0.002 m. Based on these observations, the longitudinal dispersivity used in the model was increased asymptotically from 0.05 to 0.96 m and transverse dispersivity was held constant at 0.005 m as the simulated cloud moved through the aquifer. To keep the Peclet number less than 4 and the transverse spacing less than 10 times the transverse dispersivity in the zone through which the solute cloud passed (Voss, 1984, p. 232-233), the length of the elements increased from 0.2 to 3.5 m in the direction of flow, and the height of the elements increased from 0.15 m in the area through which the cloud passed to 6.0 m below the transport zone.

Aquifer characteristics were similar to those reported in LeBlanc and others (1991) and Hess and others (1992). An ambient, steady, horizontal velocity of 0.42 m/d (meters per day) was established by specifying a hydraulic conductivity of 110 m/d, an effective porosity of 0.39, an appropriate fluid flux along the left boundary of the model based on an estimate of flow from areas upgradient from the modeled area, and appropriate pressures along the downgradient (right side) of the model. A value of 0.83 was used for the ratio of vertical to horizontal hydraulic conductivity (Hess and others, 1992).

The top and bottom of the model were specified as zero-flux boundaries. About 60 cm of recharge from precipitation was added intermittently during the simulation to the top row of elements (fig. 2). The amount and temporal distribution of recharge were determined from a water balance calculated by the method of Thornthwaite and Mather (1957) from estimates of evapotranspiration rates and measurements of precipitation at a weather station 1.8 kilometers from the site.

The simulation began with the instantaneous release of a solute cloud that was 1.8 m high and 3.4 m long. The center of the cloud was initially located 5.6 m from the left boundary of the model and 1.3 m from the top boundary. The initial tracer cloud had a dimensionless relative concentration (concentration in the ground water divided by the concentration in the initial tracer solution) of 1.0 and a fluid density of 1.00037 g/cm³, whereas the ambient ground water, inflow along the left boundary, and recharge from precipitation had a relative concentration of 0.0 and a fluid density of 0.999409 g/cm³. The solute cloud was simulated for 237 days with 191 time steps that increased during the simulation period from 0.2 to 4.5 days. Small time steps were used early in the simulation to minimize numerical dispersion (Voss, 1984, p. 234). The spatially constant longitudinal dispersivity was increased in a stepwise fashion from 0.05 to 0.96 m by stopping the simulation at appropriate times, entering the new value of dispersivity, and continuing the simulation.

Spatial moments of the simulated concentration distributions were calculated for each time step by numerical integration of concentrations using bilinear interpolation across the model elements. The moments of the simulated distributions were then compared to the moments of the observed concentrations reported by Garabedian and others (1991). In this study, the first moment in the vertical direction is used to show the vertical position, or the altitude, of the center of mass of the simulated and observed tracer clouds.

Simulated Movement of the Tracer Cloud

The simulated downward movement of the tracer cloud is compared to the observed downward movement in figure 2. The simulated downward movement after 237 days was 2.1 m, or about two thirds of the observed movement. About 40 percent (0.9 m) of the simulated downward movement occurred during the first 37 days of the simulation. Because there was no precipitation during this period, no recharge was added to the model and all of the downward movement was caused by the density difference between the tracer cloud and the ambient ground water. The rate of downward movement was greatest early in the test, when the density difference was largest, and decreased with time as dilution of the tracer cloud by dispersion decreased the density difference.

After 37 days of transport, the additional downward movement caused by the density difference was small compared to the downward movement caused by recharge from precipitation. The simulated downward movement between 37 and 237 days (1.2 m) is consistent with the total recharge applied to the top row of the model (0.45 m) during this period and a porosity of 0.39 (LeBlanc and others, 1991). The downward movement because of recharge is most evident between 37 and 45 days after the start of the tracer test, when recharge from two intense storms caused the simulated center of mass to move downward about 0.4 m.
DISCUSSION

The difference between the observed (3.2 m) and simulated (2.1 m) downward movement may be due, in part, to simulation of the tracer test in two dimensions. LeBlanc and Celia (1991) used an analytical model (Yih, 1965) to show that density-induced downward movement predicted by two-dimensional models may be about 25 percent smaller than that obtained from three-dimensional models. A two-dimensional model constrains movement of water to a two-dimensional plane, and the solute body cannot sink as rapidly as it would if the ambient ground water were free to move in any direction.

The difference between the observed and simulated downward movement may also be due, in part, to inaccurate specifications of aquifer properties and tracer-test conditions. LeBlanc and Celia (1991) demonstrated that the downward movement is very sensitive to the rate at which concentrations in the tracer cloud are diluted by dispersion. If the asymptotic value of longitudinal dispersivity (0.96 m) reported by Garabedian and others (1991) had been used for the entire simulation period, dispersion would have quickly decreased maximum concentrations and limited the amount of vertical movement. A dispersivity that increases from an initially small value to the asymptotic value is needed to represent accurately the relation between density-induced sinking and dilution by dispersion. LeBlanc and Celia (1991) also showed that the rate of downward movement is sensitive to the anisotropy of hydraulic conductivity. The amount of downward movement decreases as the aquifer becomes more permeable in the horizontal direction than in the vertical direction because flow occurs preferentially in the direction of highest permeability.

The size and shape of the initial tracer cloud also affect the amount of downward movement. LeBlanc and Celia (1991) showed that high concentrations persist longer in larger clouds than in smaller clouds; as a result, the centers of mass of larger clouds tend to sink farther than those of small clouds with the same initial density. Several preliminary simulations during this study demonstrated, however, that clouds that are short horizontally tend to sink farther than clouds that are long horizontally because the ambient ground water moves more easily around the shorter clouds as the clouds move downward because of the density difference.

The density difference directly affects the rate of downward movement. The initial densities of the tracer cloud and the ambient ground water were estimated from the concentrations of dissolved solids in the uncontaminated ground water and the tracer solution. The effects of sewage contamination beneath the site and chemical reactions involving reactive solutes in the tracer cloud (LeBlanc and others, 1991) on the density difference were not considered in this analysis.

Several preliminary simulations during this study demonstrated that the specification of model boundaries also affects the amount of downward movement. The rate of downward movement increases when the top boundary of the model is represented as a specified-pressure boundary rather than as a zero-flux boundary. As the tracer cloud sinks, the ambient water is replaced more easily by flow across the specified-pressure boundary than by flow up and around the sinking cloud when a zero-flux boundary is used. The proper representation of the water table as a specified-pressure or zero-flux boundary needs further examination.

SUMMARY

A numerical, finite-difference, solute-transport model was used to test the hypothesis that the downward movement of a tracer cloud observed during a natural-gradient tracer test in sand and gravel on Cape Cod, Mass., was caused by density-induced sinking. The model included an asymptotically increasing dispersivity, an anisotropic hydraulic conductivity, and intermittent recharge from precipitation.

The simulated downward movement after 237 days was 2.1 meters, which is about two thirds of the observed downward movement (3.2 m). The density-induced downward movement was most important during the first 37 days of transport when the density contrast between the ambient ground water and the tracer cloud was greatest.

The difference between the simulated and observed downward movement may be due, in part, to the simulation of the test with a two-dimensional model, which was shown by LeBlanc and Celia (1991) to predict less downward movement than a three-dimensional model. The difference between the observed and simulated downward movement may also be due, in part, to inaccurate specifications of
aquifer properties, such as dispersivity and anisotropy of hydraulic conductivity; and tracer-test conditions, such as the size and shape of the initial tracer cloud and the type of boundary used to represent the top of the model.

REFERENCES


Effects of Changes in Aquifer Properties on Simulated Fluid-Particle Pathlines, Cape Cod, Massachusetts

By John P. Masterson and Donald A. Walter

Abstract

A ground-water-flow model is being developed by the U.S. Geological Survey (USGS) to estimate the paths of contaminants from the Massachusetts Military Reservation and, in particular, to determine whether these contaminants will affect public-supply wells, ponds, streams, and coastal embayments.

Preliminary model results determined by use of the regional-scale flow model of western Cape Cod developed by the USGS indicate that the pathlines of contaminants emanating from the infiltration beds of the Massachusetts Military Reservation sewage-treatment plant do not coincide with the known extent of the contaminant plume. Modifications to aquifer properties simulated by the model result in a similar head distribution and stream-discharge rates for the aquifer, yet markedly different contaminant pathlines. Therefore, calibration simply based on head and stream-discharge matching is insufficient for transport analysis. Accurate calibration might require the incorporation of contaminant information to use ground-water-flow models as tools for predicting plume migration.

INTRODUCTION

Recent investigations at the Massachusetts Military Reservation (MMR) indicate that contaminated ground water is migrating from the reservation from suspected contamination sites (ABB Environmental Services Inc., 1992). The National Guard Installation Restoration Program began investigating potential problems related to suspected past releases of toxic and hazardous material at the MMR in 1986. Several questions remain unanswered concerning ground-water supply and contamination near the MMR. These questions include (1) what is the predicted path of contaminants from sources on the base; (2) what is the source of water to specific wells, ponds or streams; and (3) how will proposed activities, such as water-supply development or ground-water withdrawals for remediation affect ground-water flow and associated contaminant migration?

The answers to these questions require an understanding of the complex interaction of factors affecting ground-water flow, including recharge, ground-water withdrawals, aquifer structure and properties, and hydrologic boundaries, such as ponds and streams. Ground-water-flow models that can integrate the effect of these factors are valuable tools for addressing these questions.

The USGS, in cooperation with the National Guard Bureau, is developing a three-dimensional ground-water-flow model using MODFLOW (McDonald and Harbaugh, 1988) with a particle-tracking routine, MODPATH (Pollock, 1989), to investigate ground-water flow and advective transport near the MMR. In a recently completed investigation, Masterson and Barlow (1994) developed a regional-scale flow model that encompassed the flow cell of the western part of Cape Cod (including the MMR) to determine the effects of future ground-water withdrawals on ground-water flow. This regional flow model provides an opportunity to examine the effects of changes in aquifer properties on particle pathlines near the MMR and the boundary conditions necessary for the development of the more refined MMR model. This paper presents preliminary results of the effects of changes in aquifer properties on particle pathlines.

HYDROGEOLOGIC SETTING

The location of the study area is shown in figure 1. The area of interest is located on a broad southward-sloping glacial outwash plain known as the Mashpee Pitted Plain. The outwash plain is bounded by moraine to the north and west, by an adjacent outwash plain to the east, and by Vineyard Sound to the south. There are numerous collapse structures and kettle ponds within the outwash plain. The outwash consists of glacial silts, sands and gravels. The sediments were deposited during the Pleistocene epoch as part of a delta deposited into a large, proglacial lake that formed to the south of the retreating Laurentide ice sheet. These glacial deposits can be divided into top-set, fore-set, and bottom-set deposits (Byron Stone, U.S. Geological Survey, oral commun., 1993). Top-set deposits consist of glaciofluvial outwash deposits of coarse sand and gravel. The underlying fore-set deposits are glaciolacustrine sediments that consist primarily of medium to fine sand. Bottom-set deposits are glaciolacustrine deposits consisting of fine sand and silt. Grain size of all three depositional units decreases to the south with increasing distance from the sediment source. The deltaic sediments are underlain locally by glacial till consisting primarily of silt and clay. A hydrogeologic section through the glacial sediments is shown in figure 2. The upper 70 to 200 feet of sediment are distal top-set and proximal fore-set deposits that consist of stratified medium to coarse sand and gravel. Underlying these deposits are bottom-set deposits consisting of fine sand and silt. Thickness of the bottom-set deposits ranges from 125 to 200 feet in the study area; these deposits are underlain by glacial till. The unconsolidated sediments are underlain by granodiorite bedrock.

The flow system of western Cape Cod is bounded by saltwater to the north, south, and west, and by a regional ground-water divide to the east. Precipitation is the sole source of recharge to the ground-water system. The ground-water system is bounded at depth by bedrock, which is assumed to have a much lower permeability than the overlying sediments. Ground-water discharges primarily to streams and coastal saltwater embayments. The flow system is characterized by radial ground-water flow from a water-table mound to the north of the study area that has a maximum head of approximately 70 ft above sea level.

The direction of regional ground-water flow is approximately southward in the study area. Ground-water flow is locally influenced by kettle ponds that create a flow-through condition in which shallow ground-water discharges to the upgradient ends of the ponds and recharges the aquifer at the downgradient ends of the ponds. Ground water deeper in the flow system flows beneath the ponds. Some ponds, such as Johns and Coonamessett Ponds, have outlets that allow for limited surface outflow. The streams located in western Cape Cod are primarily gaining streams that receive their water from kettle-pond outflow and ground-water discharge.

Estimated hydraulic conductivities for the sand and gravel deposits typically range from 125 to 250 ft/d with values as high as 380 ft/d. Horizontal hydraulic conductivities of the fine sands and silts range from 30 to 125 ft/d (Masterson and Barlow, 1994).

METHODS AND RESULTS

The original three-dimensional steady-state ground-water-flow model developed for western Cape Cod (Masterson and Barlow, 1994) consists of five layers that extend from the water table to the bedrock surface with a horizontal grid spacing of 1,320 by 1,320 ft. A particle-tracking routine, MODPATH (Pollock, 1989), was coupled with this flow model to determine the effects of changes in aquifer properties on one of the plumes emanating from the MMR. This plume (Ashumet Valley plume) is the result of secondary-treated effluent discharged to the MMR sewage-treatment-plant infiltration beds since 1936. The plume extends approximately 12,500 ft south of the reservation boundary and is approximately 3,500 ft wide and 80 ft thick (ABB Environmental Services Inc., 1992).

In the model analysis, 25 particles were started at the water table in each of the two nodes that contain the sewage-treatment-plant disposal beds. Fifty particles were used because they were found to delineate pathlines emanating from the infiltration beds adequately.

Particle pathlines from the original model following the known path of the plume near the source are shown in figure 3; the eastern-most particles discharge to Ashumet Pond. However, away from the source, pathlines bend to the southeast, beneath the Childs River and Johns Pond and discharge to the Quashnet River. This configuration does not coincide with the known extent of the plume in 1988 (fig. 3a).
Figure 1. Study area on southwestern Cape Cod, Massachusetts, showing location of section A-A'.
(ABB Environmental Services Inc., 1992). In cross-section (fig. 4a), particle pathlines are shown to descend to the lowest active layer in the flow system (240 ft below sea level) before discharging upward to the Quashnet River. The known plume extent in vertical profile has a maximum depth of approximately 80 to 100 ft below sea level.

A close examination of the local geology of the study area indicates the presence of a contact between coarse-grained deltaic fore-set beds and the fine sand and silt bottom-set beds at about 70 ft below sea level (the boundary between layers 2 and 3) (fig. 2); this contact was not adequately simulated in the regional model and, thus, the model had to be adjusted. To account for this contact between coarse- and fine-grained sediments, the vertical conductance between model layers 2 and 3 was decreased from 0.002 to 0.0002, and the horizontal hydraulic conductivity was increased in layers 1 and 2 from 200 to 350 ft/d, and decreased in layers 3 to 5 from 75 to 30 ft/d. These adjusted values are within the ranges of those reported by LeBlanc and others (1988), Barlow and Hess (1993), and Masterson and Barlow (1994), for the study area. As a result of these adjustments, most of the ground-water flow is confined to the upper 100 ft of saturated material.

Figure 2. Hydrogeologic section A-A' showing location of observation wells in the study area, Cape Cod, Massachusetts.
Figure 3. Simulated head contours, particle pathlines and known extent of Ashumet Valley plume in 1988 (a) original model results (b) adjusted model results.
A second simulation was then made using the adjusted model with the same particle-starting locations. The particle pathlines of the adjusted-model simulation (fig. 3b) coincide more closely with the extent of the observed plume. The vertical profile shown in figure 4b illustrates that the depth of the pathlines coincides with the depth of the contact between the coarse and fine sediments shown in figure 2 and is consistent with the known vertical extent of the plume.

Despite significant adjustments made to the aquifer properties of the calibrated flow model, the error (root mean squared error/maximum drop in head within the study area) in calculated heads in the adjusted model was 6 percent as compared to an error in head of 3 percent in the original flow model. In addition, calculated stream discharge rates in the adjusted model were similar to those of the original model. The two models produced very different particle pathlines, although both models would be considered calibrated on the basis of head distribution and stream-discharge rates.

**SUMMARY AND CONCLUSIONS**

Preliminary simulations using an existing three-dimensional regional ground-water-flow model improve our understanding of the ground-water flow system near the MMR and will aid in the development of a fine-scaled MMR flow model. The effects of adjustments to model-calibrated aquifer properties on simulated particle pathlines illustrates how two ground-water-flow models with substantially different model input data sets can produce similar head distributions and stream-discharge rates, yet very different particle pathlines. This observation can be attributed to model calibration that is commonly based solely on water levels and stream discharge in the absence of data on ground-water velocities or extents of known plumes. Model calibration based simply on head and stream-discharge matching is insufficient for purposes of transport analysis and might require the incorporation of water-quality data to use ground-water-flow models as tools for predicting plume migration.
Figure 4. Particle pathlines projected along column 36 of the model determined by (a) simulation of original model and (b) simulation of adjusted model. Line of section shown in figure 3.
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Overview of Research Activities on the Transport and Fate of Chlorinated Solvents in Ground Water at Picatinny Arsenal, New Jersey, 1991-93

By Thomas E. Imbrigiotta and Mary Martin

Abstract

The U.S. Geological Survey is conducting an interdisciplinary research study of ground-water contamination by chlorinated solvents, particularly trichloroethylene (TCE), at Picatinny Arsenal in north-central New Jersey. This paper summarizes the results of ongoing research studies investigating the processes of desorption, volatilization, and biotransformation and their effects on the fate and transport of TCE in the ground-water system.

Results of flow-through column experiments showed that contaminated aquifer sediments can act as a continuing source of TCE to the ground water. A one-dimensional model was developed to simulate the column desorption results. The model simulates an initial, fast-stage desorption by an equilibrium process and a second, slower-stage desorption by a kinetic mechanism. Concentrations of TCE sorbed to soil did not differ significantly whether the samples were air dried overnight prior to methanol extraction or whether the extraction was conducted on wet samples and the results were corrected for the TCE content of the soil moisture.

Results of a field experiment to study the dynamics of TCE volatilization in the unsaturated zone during infiltration indicated that an equilibrium distribution of TCE between soil gas and soil water was not achieved. A two-phase transport model of gas and aqueous phases was capable of simulating the field soil-gas and soil-water TCE concentrations after modification to include a constant-flux term for desorption of TCE from soil to water.

Anaerobic biotransformation rates calculated on the basis of measured field TCE concentrations and estimated ground-water travel time between sites generally were greater than those previously measured in laboratory soil microcosm experiments.

A reactive two-dimensional multispecies transport model is being used to simulate desorption, volatilization, and microbial degradation of TCE along the central axis of the plume by using rates estimated from results of other studies at the site. The formation and transport of TCE degradation products cis-1,2-dichloroethylene and vinyl chloride also are simulated.

Aerobic cometabolic biotransformation of TCE and cis-1,2-dichloroethylene can be stimulated in soil microcosms constructed with soils from the unsaturated zone near Building 24 at the arsenal if the indigenous methanotrophic bacteria are supplied with appropriate amounts of oxygen, methane, and nutrients.

Preliminary results of a study to determine whether surfactants can enhance the removal of TCE from aquifer sediments during pump-and-treat remediation indicate that addition of the non-ionic surfactant Triton-X 100 is effective in artificially increasing the rate of mass transfer of TCE from soil to the aqueous phase.

INTRODUCTION

The U.S. Geological Survey is conducting an interdisciplinary research study of ground-water contamination by chlorinated solvents and other
contaminants at Picatinny Arsenal in north-central New Jersey. The objectives of the study are to (1) identify and quantify the chemical, physical, and biological processes that control the movement and fate of these contaminants, particularly trichloroethylene (TCE), in the subsurface; (2) determine the relative importance of these processes in transporting TCE through the ground-water system; and (3) develop predictive models of contaminant transport.

From 1960 to 1981, the wastewater-treatment system in Building 24, which housed a metal-plating facility, discharged wastewater daily into two 8-ft-deep, sand-bottomed settling lagoons behind the building (fig. 1) (Benioff and others, 1990). The wastewater contained trace metals, other inorganic ions used in plating solutions, and degreasing solvents (Imbrigiotta and Martin, 1991). From 1973 to 1985, solvent vapors from a degreasing unit were allowed to condense in an improperly installed overflow pipe and discharged into a 4-ft-deep dry well in front of Building 24. TCE was the degreasing solvent used from 1960 to 1983. The infiltration of wastewater from the lagoons and chlorinated solvents from the dry well has created a plume of contaminated ground water down-gradient from Building 24.

This paper (1) briefly describes the hydrogeology and current ground-water contamination at the Building 24 research site at Picatinny Arsenal, (2) presents and discusses a preliminary solute-transport mass balance for dissolved TCE in the shallow aquifer at the arsenal, and (3) summarizes the significant findings of the ongoing research studies at the Building 24 research site at the arsenal.

HYDROGEOLOGY AND GROUND-WATER CONTAMINATION

Picatinny Arsenal is located in a glaciated valley. The contamination plume at the Building 24 site is in a 50- to 70-ft-thick unconfined aquifer consisting primarily of coarse to fine sand with some gravel and some discontinuous silt and clay layers. On the basis of results of aquifer-test analysis and the calibration of a multilayered ground-water-flow model, the horizontal hydraulic conductivity of the unconfined aquifer is estimated to be 50 to 360 ft/d and the estimated ratio of horizontal to vertical hydraulic conductivity is 100 to 1 (L.M. Voronin, U.S. Geological Survey, written commun., 1993).

Long-term water-table altitudes average about 696 ft above sea level at Building 24, the contaminant source area, and about 686 ft above sea level at Green Pond Brook, the natural ground-water discharge point for the site. The general flow pattern in the unconfined aquifer is south-southeast from the edge of the glacial sediments to Green Pond Brook, with a slight down-valley component. Within the unconfined aquifer, flow generally is horizontal, with some downward flow near Building 24 and upward flow near Green Pond Brook. Estimated ground-water-flow velocities, based on calibrated flow-model hydraulic conductivities and measured head gradients, are about 1 to 3 ft/d in the plume area.

Ground-water contamination measured in the unconfined aquifer in 1987 and 1989 has been described previously by Sargent and others (1990) and Imbrigiotta and others (1991). Results of these studies showed that TCE was the most widespread organic contaminant in the system. Results of analyses of water samples collected from 53 wells in October and November 1991 confirmed that the areal extent of the TCE contaminant plume had changed little since the 1987 synoptic sampling (fig. 1a). The plume extends 1,640 ft from Building 24 to Green Pond Brook, where it is about 1,000 ft wide. The plume area in which TCE concentrations are greater than 10 μg/L is estimated to cover 1.4 x 10^6 ft^2. The vertical distribution of TCE along the central axis of the plume (fig. 1b) indicates that the highest concentrations (> 10,000 μg/L) still are found near the base of the unconfined aquifer midway between Building 24 and Green Pond Brook. TCE concentrations greater than 1,000 μg/L are present immediately downgradient from the source area. In 1991, TCE concentrations in water samples from most wells at the site are similar or slightly lower than those found previously.

The total estimated mass of dissolved TCE was calculated from results of six sets of synoptic water-quality analyses of samples collected during 1987-91. The estimated mass of dissolved TCE within the plume below the water table is about 1,000 kg. This mass is equal to about 660 L of pure TCE. The estimate of the mass of dissolved TCE within the plume appears to depend on the number of samples in which TCE concentrations exceeded 10,000 μg/L and the volume of ground water each of these samples is assumed to represent. As much as 60 to 70 percent of the total mass of dissolved TCE in the plume was estimated to be associated with wells in which TCE concentrations exceeded 10,000 μg/L.
A. Areal extent of trichloroethylene contaminant plume

**EXPLANATION**

- **Area in which trichloroethylene concentration exceeds 10 micrograms per liter**
- **LINE OF EQUAL TRICHLOROETHYLENE CONCENTRATION**—Shows trichloroethylene concentration, in micrograms per liter. Dashed where approximate

**A-A’** Line of section
- Sampling site location

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B. Vertical distribution of trichloroethylene concentrations

**EXPLANATION**

- **LINE OF EQUAL TRICHLOROETHYLENE CONCENTRATION**—Shows trichloroethylene concentration, in micrograms per liter. Dashed where approximate
- **Well screen and trichloroethylene concentration, in micrograms per liter**
- **NS** Not sampled
- **<** Less than

**CAF-7** Location of well and local identifier

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**Figure 1.** (A) Location of Building 24 study area at Picatinny Arsenal, New Jersey, and areal extent of trichloroethylene plume and (B) vertical distribution of trichloroethylene concentrations, October-November 1991. (Location of section A-A’ is shown in figure 1 (A).
ESTIMATED MASS DISTRIBUTION OF TRICHLOROETHYLENE AND PRELIMINARY SOLUTE MASS BALANCE

TCE may be present at the Building 24 research site in several phases: dissolved in water, as a vapor in the soil gas, and sorbed onto solid surfaces or associated with biota. TCE also may be present as a dense nonaqueous-phase liquid (DNAPL). No estimate of the amount of DNAPL TCE at the site has been made, however. The amounts of TCE in the dissolved, sorbed, and vapor phases for a block of aquifer and unsaturated zone immediately downstream from Building 24 were estimated on the basis of actual measurements of TCE concentrations in samples of all three phases (fig. 2). Most of the mass of TCE in the system near Building 24 is associated with the sediments in both the unsaturated and saturated zones.

A conceptual model of the physical, chemical, and biological processes that affect the transport and mass balance of TCE within the plume has been developed and presented previously by Imbrigiotta and Martin (1991). The physical processes of advection and dispersion in the saturated zone affect the movement of dissolved TCE and cause TCE to be removed from the system in the discharge to Green Pond Brook. TCE also is removed from the system by the biological process of anaerobic biotransformation (reductive dehalogenation) and the chemical processes of volatilization at the water table and sorption to saturated-zone sediments. Desorption of contaminated sediments can act as a source of TCE to the ground-water system. If TCE is present as a DNAPL, dissolution will result in an increase in dissolved TCE in the ground water.

Preliminary estimates of the fluxes of processes that affect the mass balance of TCE within the ground-water system at the Building 24 site are shown in figure 3. The estimated flux of TCE discharged to Green Pond Brook from the plume area, on the basis of measurements of TCE concentrations in ground water and base-flow discharge to the brook, is 1 to 2 mg/s. The flux of TCE volatilized from the water table is estimated to be about 0.1 mg/s on the basis of measured soil-gas TCE gradients and estimates of the physical characteristics of the unsaturated zone. Although volatilization appears to be a minor factor affecting the mass balance of TCE in the ground-water system, Martin (this volume) states that results of a modeling sensitivity analysis show volatilization to be an important mechanism for removing solutes and thereby affecting concentrations near the water table. Biotransformation probably is the mechanism by which most dissolved TCE leaves the ground-water system. First-order rate constants for TCE transformation ranging from less than 0.001 to 0.02/wk were estimated by Wilson and others (1991) on the basis of laboratory microcosm studies of soil from five sites within the plume area. By using the estimated mass of dissolved TCE, the flux of TCE lost from the plume through biotransformation is calculated to be in the range of 1 to 30 mg/s. Analogous first-order rate constants for TCE biotransformation calculated by Ehlke and others (1996) from field-measured TCE concentrations and time-of-travel data generally were higher than those measured in the laboratory experiments. Thus, the flux of TCE lost through biotransformation may actually be greater than that shown in figure 3.

Desorption of TCE from soils that have undergone long-term adsorption (years) and dissolution of DNAPL TCE probably are the processes by which most TCE enters the ground-water system. Because no estimate of the amount of DNAPL TCE has been made, no estimate of TCE dissolution can be made. Three first-order rate constants of TCE desorption from shallow aquifer sediments at the arsenal made by Koller and others (1996) ranged from 0.003 to 0.015/wk. By assuming the estimated mass of TCE sorbed to the aquifer sediments to be three to four times the mass of TCE in the dissolved state, the estimated flux of TCE into the ground-water system through desorption is in the range of 15 to 85 mg/s. The rate constants were measured in laboratory flow-through columns by using uncontaminated water as the influent fluid. Desorption rates in the field probably would be lower where ground water containing TCE is flowing past the desorbing sediments. This flux estimate is made by assuming that, over long periods (years), the short-term desorption rate (weeks and months) is equal to the short-term adsorption rate.

CURRENT RESEARCH ACTIVITIES

The ongoing studies at the Picatinny Arsenal site fall into five major areas of research: (1) chemical processes affecting transport of chlorinated solvents in the saturated zone, (2) transport of chlorinated solvents in the unsaturated zone, (3) biotransformation of chlorinated solvents in the saturated zone, (4) solute-transport modeling of chlorinated solvents in the
MASS DISTRIBUTION OF TRICHLOROETHYLENE NEAR BUILDING 24
[kg, kilogram; <, less than; >, greater than; %, percent]

<table>
<thead>
<tr>
<th>Unsaturated Zone</th>
<th>Gas</th>
<th>0.001 kg</th>
<th>&lt;0.1%</th>
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<td>Soil</td>
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<table>
<thead>
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<th>1 kg</th>
<th>20%</th>
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<tr>
<td></td>
<td>Soil</td>
<td>4 kg</td>
<td>80%</td>
</tr>
</tbody>
</table>

Figure 2. Mass distribution of trichloroethylene in the saturated and unsaturated zones immediately downgradient from Building 24 at Picatinny Arsenal, New Jersey.
saturated zone, and (5) remediation processes for chlorinated solvents in the saturated and unsaturated zones. A brief summary of the current research findings on each of these subjects is given in the following sections.

**Chemical Processes Affecting Transport of Chlorinated Solvents in the Saturated Zone**

Flow-through columns were constructed with sediments from four sites within the TCE plume to determine the rate of TCE desorption in the saturated zone. Desorption appeared to occur at all sites in two stages—an initial, rapid stage (days to weeks) during which 1 to 10 percent of the total sorbed mass of TCE was released, followed by a slow stage (months to years) during which the remaining 90 to 99 percent was desorbed. A column experiment with sediment artificially contaminated in the laboratory for only 5 days showed the same two-stage desorption, but 65 to 70 percent of the TCE mass was desorbed in the initial, rapid stage, and the remaining 30 to 35 percent...
was desorbed in the slow stage. A one-dimensional model was developed to determine the desorption rates by simulating the concentrations measured in the desorption column experiments. Results of the model simulations compared well with the column data by simulating initial, fast-stage desorption as an equilibrium process and a second, slower-stage desorption as a kinetic process. Model-calculated long-term (slow-stage) desorption rates of TCE from Picatinny Arsenal soils ranged from $0.5 \times 10^{-8}$ to $2.5 \times 10^{-8}$/s.

The effect of air drying TCE-contaminated soils prior to extraction with methanol to determine the concentrations of sorbed TCE was investigated. Aquifer-sediment samples collected at five locations within the TCE plume were split into two fractions; one fraction underwent extraction while wet and the other underwent extraction after being air-dried overnight. Concentrations of TCE in the wet soils were corrected for TCE in the soil moisture by subtracting the results of analyses of the ground-water samples. Comparison of the extraction results for air-dried and wet soils showed that, for four of the five samples, the concentration of sorbed TCE in the air-dried soils was not significantly different from that in the wet soils.

### Transport of Chlorinated Solvents in the Unsaturated Zone

A study was conducted to quantify gas-water mass-transfer rates at the low flow rates of infiltrating water encountered in the unsaturated zone at the Building 24 site. This was done by conducting a field experiment under steady-state infiltration conditions and by using a mathematical model to simulate the results. A gas- and aqueous-phase transport model with desorption simulated as a constant-flux source of TCE at all depths was capable of simulating the field data. The gas-water mass-transfer rate constant used in the model was $4.5 \times 10^{-6}$/hr. Equilibrium between the gas- and water-phase concentrations of TCE was not observed during infiltration at the field site. Mass-transfer limitations between the soil-water and soil-solid phases also were observed during infiltration.

### Biotransformation of Chlorinated Solvents in the Saturated Zone

Rates of anaerobic biotransformation of TCE and cis-1,2-dichloroethylene (cisDCE) were estimated by using field measurements from selected sites along a flow path in the plume and time of travel for ground water between the sites. The first-order biotransformation rates for TCE calculated in this manner ranged from less than 0.001 to 0.08/wk, whereas the first-order biotransformation rates for cisDCE ranged from less than 0.001 to 0.03/wk. The field-calculated biotransformation rates for TCE generally were more rapid than the biotransformation rates measured previously in the laboratory soil microcosms (<0.01 to 0.02/wk) (Wilson and others, 1991). Field-calculated biotransformation rates for cisDCE generally were lower than the biotransformation rates measured in laboratory soil microcosms (<0.01 to 0.18/wk) (Ehlke and others, 1991). These results show that field TCE-concentration data and time-of-travel data can yield biotransformation-rate estimates for TCE and cisDCE that are usually the same order of magnitude as those measured in laboratory soil-microcosm studies.

### Solute-Transport Modeling of Chlorinated Solvents in the Saturated Zone

A modified version of the USGS SUTRA transport code (Voss, 1984) is being used to simulate areally variable desorption, volatilization at the water table, and microbial degradation of TCE. The transport of degradation products, cisDCE and vinyl chloride, also is simulated. The reactive multispecies solute-transport code was previously described by Martin (1991). The modified code simulates the transport and reaction of any number of species at the same time.

Sensitivity simulations with higher simulated ground-water velocities than those in the calibrated model generally resulted in increased simulated concentrations of TCE and decreased simulated concentrations of the degradation products. Sensitivity analysis on dispersivity showed that the simulated concentrations were too high or too low compared to measured concentrations when dispersivity rates were other than those used in the calibrated model. Results of sensitivity simulations run with various desorption and degradation rates generally showed that use of the laboratory estimates provided reasonable simulated concentrations.
Remediation Processes for Chlorinated Solvents in the Saturated and Unsaturated Zones

The feasibility of using aerobic cometabolic biotransformation of gas-phase TCE in the unsaturated zone as a remediation process was tested. In this process TCE is degraded as a consequence of stimulating methane degradation. Soil cores were collected near the contaminant source, where the soil-gas concentration of TCE was greatest (43 µg/L), and were used to construct soil microcosms. Results of the soil-microcosm study showed that biotransformation of TCE was rapid (16 µg/L/d) in acclimated soil having a 1.2-percent methane headspace. Thus, this remediation process is feasible at the Picatinny Arsenal site and occurs at a much faster rate than anaerobic TCE biotransformation processes. Further studies to optimize the TCE, methane, oxygen, and nutrient concentrations are planned.

A study was begun to determine whether the addition of the nonionic surfactant Triton X-100 to ground water can artificially increase the rate of TCE mass transfer from aquifer sediments was begun. Soil samples from the field were used in laboratory experiments conducted with continuous-flow stirred tank reactors, with and without Triton X-100. Preliminary results indicate that the rate of desorption is increased by 15 to 20 percent by the presence of Triton X-100 in the aqueous phase. Two possible mechanisms that could be responsible for the increased desorption rate are proposed: (1) the addition of Triton X-100 above its critical micelle concentration increased the apparent water solubility of TCE and thus increased the concentration gradient between the sorbed and aqueous phases, or (2) the presence of Triton X-100 increased the mass-transfer coefficient. Future experiments are planned to determine precisely the mechanism affecting the rate of desorption.

SUMMARY

The results of the ongoing interdisciplinary studies at the Picatinny Arsenal research site in north-central New Jersey have been synthesized to yield preliminary estimates of the TCE mass distribution and the TCE mass balance (transport fluxes) in the ground-water system. Contaminated sediments are the primary repository for TCE in both the saturated and unsaturated zones. Desorption of TCE from contaminated sediments is a significant long-term source of TCE to the ground-water system. Anaerobic biotransformation of TCE apparently is the most important process for removal of TCE from the ground-water system. These results can be used to guide future investigations of other sites contaminated with chlorinated solvents. In addition, some of the results of the remediation studies may help in the eventual cleanup of such sites.

Plans for future work at Picatinny Arsenal include (1) determination of the presence or absence of DNAPL TCE at the site and its relative importance as a source of TCE compared to desorption; (2) application of the modified solute-transport model to test hypotheses of plume formation, plume aging, and the expected effectiveness of different remediation processes in cleaning up the plume; (3) direct measurement of the TCE flux volatilizing through the unsaturated zone; (4) field testing of surfactants as a method to enhance desorption of TCE from contaminated sediments; (5) application of aerobic cometabolic biotransformation of TCE in the field to test its effectiveness as a remediation process at pilot scale; and (6) application and evaluation of other remediation technologies for chlorinated solvents at the field scale.

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Simulation of Transport, Desorption, Volatilization, and Microbial Degradation of Trichloroethylene in Ground Water at Picatinny Arsenal, New Jersey

By Mary Martin

Abstract

The fate of dissolved trichloroethylene in ground water at Picatinny Arsenal, New Jersey, is being analyzed using a reactive multispecies transport model of a two-dimensional vertical section along the central axis of the plume. The model simulates the desorption, volatilization at the water table, and microbial degradation of trichloroethylene. The formation and transport of the degradation products cis-1-2-dichloroethylene and vinyl chloride also are simulated. Results of this modeling analysis demonstrate the applicability and usefulness of the multispecies two-dimensional transport code to contaminant-fate and -transport studies.

INTRODUCTION

The U.S. Geological Survey (USGS) is conducting an interdisciplinary research study of the contamination of ground water by chlorinated solvents and other contaminants at Picatinny Arsenal, New Jersey. As part of the study, the fate and transport of dissolved trichloroethylene (TCE) in ground water at the arsenal are being analyzed with a reactive multispecies transport model. The transport simulations are being used to test hypotheses concerning the fate of TCE in the ground-water-flow system by using sensitivity simulations.

TCE entered the ground-water-flow system from a metal-plating facility and wastewater-settling lagoons at Building 24 at the arsenal during 1960-85 (fig. 1). TCE concentrations measured during 1985-93 were used to define a 1.4 x 10^6-ft^2 plume area extending 1,630 ft from Building 24 to Green Pond Brook in a thickness of about 60 ft of unconfined glacial sediments. The amount of dissolved TCE in the ground water within the plume area is estimated to be about 1,000 kg (about 2,200 lb) on the basis of these measurements. This mass is equal to about 175 gallons of liquid TCE. The chemistry of the ground water, measured TCE concentrations, and the chemical processes affecting the fate of TCE within the plume are discussed by Imbrigiotta and others (1988 and 1991). The model simulates transport from Building 24 to Green Pond Brook, the natural discharge area, along the approximate flow lines within the unconfined aquifer near the central axis of the plume.

A modified version of the USGS SUTRA transport code (Voss, 1984) is being used to simulate the desorption, volatilization at the water table, and microbial degradation of TCE. The formation and transport of degradation products, cis-1-2-dichloroethylene (cisDCE) and vinyl chloride (VC), also are simulated. The reactive multispecies solute-transport code is described generally in Martin (1991). The modified code retains all the simulation capabilities of the SUTRA code and also simulates the transport and reaction of any number of species. The mathematics that describe the chemical reactions must be programmed by the user.

This paper presents the results of sensitivity simulations used in testing hypotheses concerning the fate of TCE in ground water at Picatinny Arsenal. Sensitivity simulations were designed to compare simulated solute concentrations from the calibration simulation to concentrations from simulations in
Figure 1. (A) Location of Building 24 study area at Picatinny Arsenal, New Jersey, and areal extent of trichloroethylene plume and (B) vertical distribution of trichloroethylene concentrations, October-November 1991. (Location of section is shown in fig. 1A.)
which different rates were used for the various mass-balance components. Concentrations from the calibration and sensitivity simulations are compared. The applicability and usefulness of the multispecies two-dimensional transport code to analyze contaminant fate and transport is demonstrated.

**MODEL DESIGN AND CALIBRATION**

Average steady-state flow conditions within the 95,000-ft², 1-ft-wide cross-sectional area are simulated by using a grid with 14,329 nodes. Element areas range in size from 0.1 to 20 ft². Specified-flux boundary conditions are used to represent groundwater recharge and flows across the horizontal and vertical boundaries of the cross-sectional area (fig. 2). Simulated inflow at the flux boundaries is about \(7.5 \times 10^{-4}\) ft³/s and simulated outflows are about \(2.5 \times 10^{-4}\) ft³/s. The magnitudes of the simulated boundary fluxes were calculated by using simulated flows from a three-dimensional ground-water flow model of the valleywide flow system at Picatinny Arsenal (Voronin, 1991). A constant-head node is used to represent the head in Green Pond Brook where it crosses the line of section. Simulated outflow at Green Pond Brook is about \(5 \times 10^{-4}\) ft³/s. The resulting altitude of the simulated water table is 696 ft above sea level near Building 24 and 686 ft at Green Pond Brook.

Solute transport is simulated for 5 years in 50 time steps. The final simulated concentrations represent essentially steady-state plume conditions after 1985. Constant-concentration nodes and desorption within the plume area are solute sources to the simulated system. Simulations were made with constant-concentration TCE sources of 110 mg/L (one-tenth of the TCE saturation concentration) at the water table beneath Building 24 and at the base of the unconfined aquifer 770 ft downgradient from Building 24. During 1987-91, TCE concentrations in ground water within the plume have consistently been greatest at these locations (greater than 1,000 \(\mu\)g/L near Building 24 and greater than 14,000 \(\mu\)g/L near the base of the unconfined aquifer). The constant-concentration solute sources are assumed to represent high rates of desorption or dissolution of TCE near the settling lagoons, at the overflow dry well, and near the base of the unconfined aquifer 770 ft downgradient from Building 24. Nonaqueous-phase flow of TCE from Building 24 to the base of the unconfined aquifer is hypothesized as the cause of high concentrations of TCE at the base of the unconfined aquifer (Imbrigiotta and others, 1991).

![Figure 2. Schematic drawing showing conceptual solute-transport model and simulated boundary conditions.](image)
Both volatilization and microbial degradation are simulated with first-order decay rates that are a function of the simulated concentration of TCE. Microbial degradation was simulated throughout the plume area, but volatilization was simulated only at the nodes representing the water table. Desorption was simulated by using a first-order production term and was a function of the estimated amount of TCE sorbed to sediments within the plume. The rates at which these processes were simulated and the methods used to determine the rates are discussed in the following section on sensitivity analysis.

The flow system was calibrated by using heads and head gradients measured synoptically in 13 to 21 monitor wells nine times during 1987-93. Generally, heads are simulated to within 1 ft of the 1993 water-level measurements, which are most representative of average flow conditions. The solute-transport system was calibrated by matching simulated TCE, cisDCE, and VC concentrations to those measured synoptically in samples from 15 to 47 monitor wells six times during 1987-91. TCE, cisDCE, and VC concentrations generally are simulated to within an order of magnitude of average concentrations measured in micrograms per liter in water from each well. Simulated TCE, cisDCE, and VC concentrations from the calibrated model, with simulated desorption, volatilization, and microbial degradation, are shown in figure 3.

A precise calibration was not attempted because of the limitations of using a two-dimensional simulation along an estimated flow path and of estimating flow and solute-transport characteristics along the section. The model was calibrated to represent a realistic flow field and approximate concentrations within the plume. This type of calibration is consistent with the purpose of the transport simulations—that is, to test hypotheses concerning the fate of TCE in the ground-water flow system. Relatively small-scale variations in the flow and solute-transport characteristics are not expected to be represented accurately in the model. Also, this modeling approach does not provide a unique estimate of the magnitude of the mass-balance components; however, the overall characterization of the flow and transport systems, as well as the testing of hypotheses and the comparison of factors affecting the fate of TCE, is reasonable and is the most detailed and comprehensive possible within the limitations of the model design and data availability.

SENSITIVITY ANALYSIS

A sensitivity simulation in which TCE is transported as a conservative solute results in simulated TCE concentrations that are much higher than those simulated by using the calibrated model. The simulation results show desorption, volatilization, and microbial degradation to be important mass-balance components affecting TCE concentrations. Simulated TCE concentrations within the same hydrogeologic system represented in the calibrated model, but with no simulated desorption, volatilization, or microbial degradation, are shown in figure 4.

Horizontal hydraulic conductivities in the calibrated model are 150 to 320 ft/d for the sandy parts of the aquifer and 50 ft/d for the fine-grained parts of the aquifer. The ratio of simulated horizontal to vertical hydraulic conductivity is 100 to 1 throughout the section except near Green Pond Brook, where the ratio is 10 to 1. The porosity of all the sediments is 0.3. Sensitivity analysis conducted by using higher horizontal hydraulic conductivities than those in the calibrated model caused simulated concentrations to increase to unreasonable values over most of the plume area. Decreasing either the anisotropy throughout the section or the hydraulic conductivity of the fine-grained layers resulted in irregularities in the plume configuration with relatively low concentrations of TCE and relatively high concentrations of the degradation products in the fine-grained layers. Simulated flow velocities generally were 1 to 3 ft/d at the simulated location of the monitor wells. Lower simulated porosities or higher simulated hydraulic conductivities caused simulated ground-water velocities to increase, which in turn generally caused simulated TCE concentrations to increase and simulated concentrations of the degradation products to decrease.

Simulated lateral dispersivity is 1.0 ft and simulated transverse dispersivity is 0.1 ft. Results of sensitivity analysis conducted by using dispersivity values that varied one-half of an order of magnitude from those in the calibrated model indicated that lateral and transverse dispersivity values greater than 1.0 ft and 0.1 ft, respectively, cause the simulated plume orientation to be more vertical and simulated concentrations of TCE and the degradation products to increase to unreasonable values over most of the plume area. Rates of lateral and transverse dispersivity less than those used in the calibrated
Figure 3. Simulated concentrations from calibrated model with simulated desorption, volatilization, and microbial degradation: (A) trichloroethylene, (B) cis-1,2-dichloroethylene, and (C) vinyl chloride. (Location of section A-A' shown in fig. 1.)
model cause the simulated plume orientation to be more horizontal and simulated concentrations in the central part of the plume to decrease to unreasonable values.

Volatilization at the water table was simulated at a rate of $8.6 \times 10^{-6}/s$ on the basis of estimates of the physical characteristics of the unsaturated zone. Use of higher simulated rates of volatilization in the sensitivity simulations than those used in the calibrated model resulted in simulated concentrations that more closely match measured concentrations at the locations of monitor wells near the water table. Because of the model's limitations, however, estimates of volatilization based on model calibration and sensitivity are not considered to be more accurate than estimates based on physical characteristics. Results of the sensitivity analysis showed that volatilization is an important mechanism for removing solutes and thereby affecting concentrations near the water table.

Desorption, biological degradation of TCE and the formation of cisDCE, and the degradation of cisDCE and the formation of VC all were simulated at a rate of 0.005/week. Because the degradation of VC was not simulated, simulated concentrations are higher than measured concentrations. Desorption rates were estimated on the basis of results of laboratory desorption measurements made after 20 days (Koller, 1992) and degradation rates were estimated on the basis of laboratory degradation measurements (Wilson and others, 1991). Although quantification of the rates of desorption and degradation in the plume area is difficult, the processes probably control the major gains and losses of TCE. Results of sensitivity simulations conducted with various desorption and degradation rates generally show that use of the laboratory estimates resulted in reasonable simulated concentrations.

CONCLUSIONS

Although the calibrated model does not provide a unique estimate of the magnitudes of the various mass-balance components of the plume of TCE-contaminated ground water at the Building 24 site, the use of sensitivity simulations to test hypotheses concerning the fate of TCE in ground water is useful. Sensitivity simulations in which simulated ground-water velocities were higher than those in the calibrated model generally resulted in increased simulated concentrations of TCE and decreased simulated concentrations of the degradation products. Results of sensitivity analysis on dispersivity showed that the simulated concentrations were unreasonable when dispersivity rates differed from those used in the calibrated model by one-half order of magnitude. Although volatilization is not a major mass-balance
component, this process was shown to be an important mechanism in removing solutes and thereby affecting solute concentrations near the water table. Results of sensitivity simulations with various desorption and degradation rates generally showed that use of the laboratory estimates resulted in reasonable simulated concentrations.

The ability of the model to simulate concentrations of TCE and its microbial degradation products, cisDCE and VC, as well as the response of the simulated concentrations in the sensitivity simulations has provided useful insights into determining the fate of TCE in ground water at Picatinny Arsenal and analyzing the applicability of estimated physical and chemical characteristics. This modeling analysis also demonstrates the applicability and usefulness of the multispecies two-dimensional transport code to contaminant-fate and -transport studies.

REFERENCES


Simulation of Trichloroethylene Volatilization in the Unsaturated Zone during a Field Infiltration Experiment at Picatinny Arsenal, New Jersey

By H. Jean Cho¹, James A. Smith², and Peter R. Jaffe³

ABSTRACT

A field experiment was conducted at Picatinny Arsenal, New Jersey, to study the dynamics of trichloroethylene as it volatilizes from contaminated ground water to land surface during infiltration. It was found that the gas- and water-phase concentrations of TCE were not in equilibrium in the unsaturated zone during infiltration. A mathematical model was developed to simulate the volatilization of TCE in the unsaturated zone. Gas-water mass-transfer rate constants were calibrated to the data. The mass-transfer limitations of a volatile organic compound between the gas and liquid phases were described explicitly in the model. The water-infiltration rate was 0.34 centimeters per hour, and TCE desorption from the soil matrix was significant. Slow desorption of TCE from the soil matrix was incorporated in the mathematical model.

INTRODUCTION

A field experiment was conducted at Picatinny Arsenal in Morris County, New Jersey, to study the transport of trichloroethylene (TCE) in the unsaturated zone during infiltration. In 1960, TCE was the primary solvent used for metal degreasing at Picatinny Arsenal. The wastewater from the degreasing operations was discharged into sand-lined lagoons and into an overflow dry well adjacent to Building 24 (fig. 1). As a result, a plume of TCE-contaminated ground water has been formed in the unconfined aquifer that now extends from Building 24 to Green Pond Brook, the ground-water discharge point (Smith and others, 1992).

This research was conducted to study the distribution of TCE between the aqueous and gaseous phases in an unsaturated soil system and to quantify the rate of exchange of TCE between the two phases. The primary focus of the research is the movement of a volatile organic compound (VOC) which is dissolved in ground water and which diffuses upward to land surface. Specifically, the research is aimed at evaluating the effect of infiltrating water on the volatilization process. During infiltration, the VOC will tend to dissolve in the percolating water, so that mass transfer of the volatilized VOC will occur between the soil-air and soil-water phases.

The main objective of this research was to quantify gas-water mass-transfer rates at the low flow rates of infiltrating water encountered in the unsaturated zone. This was done by means of a field experiment conducted under steady-state infiltration conditions and use of a mathematical model of two-phase VOC transport.

METHODS

Mathematical Model

A model was developed to simulate the transport of a VOC in the unsaturated zone during
infiltration. The governing equations at steady state are

\[ 0 = \frac{\partial}{\partial z} \left( D_G \frac{\partial c_g}{\partial z} \right) - K_{gw} \theta_g \left( \frac{c_g}{H} - c_w \right) \]  

(1)

\[ 0 = -\frac{\partial}{\partial z} (q_w c_w) + \frac{\partial}{\partial z} \left( D_W \frac{\partial c_w}{\partial z} \right) + \frac{K_{gw} \theta_g}{H} \left( \frac{c_g}{H} - c_w \right) + S, \]  

(2)

where \( c_g \) and \( c_w \) are the concentrations of the solute in the soil gas and soil water, respectively; \( \theta_g \) and \( \theta_w \) are the volumetric soil-gas and soil-water fractions, respectively; \( q_w \) is the infiltration rate; \( D_G \) and \( D_W \) are the molecular diffusion coefficients of the solute in soil air and soil water, respectively; \( H \) is Henry's constant; \( K_{gw} \) is the gas--water mass-transfer-rate constant; and \( S \) is a constant source term describing TCE mass transfer from the soil matrix to the soil water.

Figure 1. Map of Picatinny field site and distribution of trichloroethylene in ground water.
Field Apparatus

Lysimeters for sampling soil water in the unsaturated zone were constructed from porous ceramic cups. Soil-gas samplers were constructed from stainless-steel tubing and fine-mesh stainless-steel screening (Cho and others, 1993).

The lysimeters for the field infiltration experiment were installed in March 1991 (fig. 2). Six boreholes were drilled to a depth of 4 m using a 5.1-cm-outer-diameter drive point attached to a 4.8-cm-diameter-outer pipe. The locations of these six boreholes are shown in figure 1. The water table at the site was approximately 3.5 m below land surface. A probe installed at a 3.6-m depth was used to sample shallow ground water. Above the water table, four lysimeters with 2.7-m, 2.1-m, 1.5-m, and 0.9-m lengths of tubing and four soil gas probes, with 2.4-m, 1.8-m, 1.2-m, and 0.6-m lengths of tubing, were installed. Each probe was surrounded by a mixture of sieved (no. 10 sieve) native soil and commercial fine sand (95 percent finer than 0.59 mm diameter). A bentonite layer was emplaced between probes to prevent preferential flow along the borehole. Additional boreholes was drilled for the emplacement of thermisters and a neutron probe (Cho and others, 1993) (fig. 1).

Unsaturated-zone water was collected using a 5-mL gastight syringe with a Mininert valve, as described by Smith and others (1992). When 5 mL of water had been collected, the Mininert valve was closed, a liquid field surrogate was injected into the sample, and the syringe was placed on ice in a cooler for transport to the laboratory. Soil-gas samples were collected in 125-mL gas sampling bulbs by a procedure described by Smith and others (1990). The samples were transported at room temperature in a cooler to the laboratory.

In the laboratory, soil-water samples were analyzed using a gas chromatograph with a purge-and-trap concentrator, a capillary column, and an electrolytic conductivity detector. Soil-gas samples were analyzed using a gas chromatograph with a purge-and-trap concentrator, a packed column and an electrolytic conductivity detector (Cho and others, 1993).

Results and Discussion

To maintain steady infiltration rates during the field experiment, a sprinkler was turned on at the site on June 5, 1991, and remained on until July 1, 1991. The infiltration rate remained relatively constant at approximately 0.34 cm/h, with a standard deviation of 0.15 cm/h. The moisture-content profile was determined with a neutron probe and gravimetric soil analyses. At the Picatinny field site, moisture contents stabilized after the first day of infiltration (Cho, 1992).
Although steady-state TCE concentrations were measured in gas and water samples from boreholes 6-7 and 6-8 on June 11, 12, 13, 15, and 17, only those from borehole 6-8 are discussed here. TCE concentrations from for borehole 6-7 were similar to those from borehole 6-8. One sample was collected from each gas probe and two from each lysimeter on each day of sampling. Mean TCE concentrations and standard deviations as a function of depth are shown in table 1.

Table 1. Mean concentrations of TCE in soil gas and soil water at borehole 6-8

<table>
<thead>
<tr>
<th>Depth (m)</th>
<th>Mean concentration (ug/L)</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas Probes&lt;br&gt;0.6</td>
<td>0.003</td>
<td>0.005</td>
</tr>
<tr>
<td>1.2</td>
<td>0.022</td>
<td>0.009</td>
</tr>
<tr>
<td>1.8</td>
<td>0.051</td>
<td>0.005</td>
</tr>
<tr>
<td>2.4</td>
<td>0.113</td>
<td>0.043</td>
</tr>
<tr>
<td>Lysimeters&lt;br&gt;0.9</td>
<td>0.39</td>
<td>0.20</td>
</tr>
<tr>
<td>1.5</td>
<td>0.43</td>
<td>0.17</td>
</tr>
<tr>
<td>2.1</td>
<td>0.55</td>
<td>0.23</td>
</tr>
<tr>
<td>2.7</td>
<td>0.68</td>
<td>0.23</td>
</tr>
</tbody>
</table>

Henry's constants were calculated as a function of depth using temperature measurements and the temperature-Henry's constant relation of Gossett (1987). The measured gas-phase concentrations were divided by Henry's constant to compute the water-phase concentrations expected under equilibrium conditions. Gas-phase TCE concentrations normalized with Henry's constant and observed water-phase TCE concentrations are plotted in figure 3, along with one standard deviation error bars. The dotted lines in figure 3 are linear regression lines relating both the normalized TCE concentration in soil gas and the TCE concentration in soil water to depth. Under equilibrium conditions, the normalized TCE concentrations in soil gas (triangular symbols) and the measured TCE concentrations in soil water (square symbols) would be coincident. The data in figure 3 show that the soil-water-phase TCE concentrations were higher than those predicted with the equilibrium assumption, suggesting that the soil at Picatinny Arsenal was acting as a source of TCE to the percolating soil water.

### Laboratory Desorption Experiments

In order to test this hypothesis, a series of column desorption experiments was conducted in the laboratory on soil cores collected at the outer perimeter of the site of the infiltration experiment. Significant quantities of TCE were observed in the column effluent when clean deionized water was pumped into the soil (Cho, 1992). Fluxes of TCE from the soil matrix to the soil water were calculated using the equation

\[ S = \frac{C_w q_w}{X}, \]

where \( C_w \) is the concentration of TCE in soil water which has traveled a distance \( X \) through the soil. Using equation 3 and concentration data from the soil desorption experiments, a constant \( S \) of 1.4 mg/(m²·h) was computed for the Picatinny soil.

### Numerical Simulations of Field Data

Numerical simulations of the field experiment were conducted to calibrate the steady state model of equations 1 and 2. Input parameters and boundary conditions are shown in table 2.

Table 2. Input parameters and boundary conditions for numerical simulation.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Element size</td>
<td>0.01 cm</td>
</tr>
<tr>
<td>Soil Temperature</td>
<td>20°C</td>
</tr>
<tr>
<td>Henry's constant</td>
<td>0.32</td>
</tr>
<tr>
<td>Gas concentration of TCE at upper boundary</td>
<td>0</td>
</tr>
<tr>
<td>Water concentration of TCE at upper boundary</td>
<td>0</td>
</tr>
<tr>
<td>Gas concentration of TCE at lower boundary</td>
<td>36 µg/L</td>
</tr>
<tr>
<td>Water concentration of TCE at lower boundary</td>
<td>8 µg/L</td>
</tr>
</tbody>
</table>
In an initial simulation, the source term of TCE from the soil matrix, $S$, was set at 1.4 mg/(m$^3$·h) as determined from desorption experiments. Under these conditions, the model significantly overpredicts concentrations of TCE in the soil water. A likely explanation is that the source term, $S$, obtained from desorption experiments on highly disturbed cores could not accurately predict desorption from undisturbed field soil. It was concluded that the data collected from laboratory desorption experiments could not be used to simulate the field experiments. Therefore, $S$ was added to the calibration parameters. The simulations were conducted to calibrate two parameters: $S$ to account for processes within the soil-water phase and $K_{gw}$ to account for interaction between the soil-water and soil-gas phases, which were not in equilibrium. The best-fit values of $K_{gw}$ and $S$ are shown in Table 3. The model output for borehole 6-8 is shown in Figure 4. In all three plots, the estimated soil-moisture content is shown by a dotted line. In this simulation, both (a) the observed concentrations of TCE in soil water and (b) the observed concentrations of TCE in soil gas were fairly well matched by the model (solid line). The third plot in Figure 4 shows the degree of disequilibrium, defined as the ratio of the concentration of TCE in the soil gas to the concentration of TCE in the soil water divided by Henry's constant. At equilibrium, the degree-of-disequilibrium is one. The dashed line in the degree of disequilibrium plot denotes equilibrium conditions. Throughout the unsaturated zone, the degree of disequilibrium was less than one, indicating

Table 3. Parameters for numerical simulation of field data for borehole 6-8

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Best fit value</th>
<th>Standard deviation of estimate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas-water mass transfer-rate constant, $K_{gw}$ (h^{-1})</td>
<td>$4.5 \times 10^{-6}$</td>
<td>$1.0 \times 10^{-5}$</td>
</tr>
<tr>
<td>TCE flux from soil matrix to soil water, $S$, (\mu g/(m^3\cdot h))</td>
<td>1.6 $\mu g/(m^3\cdot h)$</td>
<td>0.4 $\mu g/(m^3\cdot h)$</td>
</tr>
</tbody>
</table>

**Figure 4.** Measured and predicted trichlorethylene concentrations and degree of disequilibrium for Borehole 6-8.
that the concentration of TCE in the soil gas was less than the concentration predicted based on equilibrium with the aqueous phase.

**Summary**

A field experiment was conducted at Picatinny Arsenal, where TCE has contaminated an unconfined sand and gravel aquifer. A desorption experiment on field soils showed that a considerable amount of TCE has sorbed to the soil matrix. Therefore, there were two sources of TCE to unsaturated soil gas and soil water: TCE from the contaminated ground water and TCE sorbed onto unsaturated-zone soils. As a first approximation, the source of TCE from the soil matrix to the soil water was treated as a constant-flux term for soil water at all depths. Using this term, a two-phase transport model, originally developed to treat only the gas and aqueous phases of a VOC, was capable of simulating the field data, with a best fit $K_{gw}$ of approximately $10^{-6}$ h$^{-1}$.

The equilibrium distribution of TCE between the soil-water and soil-gas phases was not achieved during infiltration experiments at the Picatinny site. Mass-transfer limitations between the soil-water and soil-solid phases also were observed during. Because of the importance of desorption, a precise value of $K_{gw}$ was difficult to obtain in the field, and the calibrated value was not significantly different from zero.

Nevertheless, the low $K_{gw}$ values obtained show that equilibrium conditions were not met during the experiments.

**REFERENCES**


Cometabolic Biotransformation of Trichloroethylene and cis-1,2-Dichloroethylene in Unsaturated-Zone Soil at Picatinny Arsenal, New Jersey

By Theodore A. Ehlke and Thomas E. Imbrigiotta

Abstract

This study determined the feasibility of in situ cometabolic remediation of gas-phase chlorinated ethenes at Picatinny Arsenal, New Jersey. Cometabolic biotransformation of trichloroethylene (TCE) and cis-1,2-dichloroethylene (cis-DCE) was studied in a laboratory experiment with unsaturated-zone soil cores collected within a contaminant plume near the source. Concentrations of TCE and cis-DCE in soil, soil gas, and ground water within the plume also were quantified. At the highest concentrations studied, TCE (3.2 μM) mixed with cis-DCE (4.3 μM) was degraded most rapidly (0.05 μmol TCE/L/d, 0.09 μmol cis-DCE/L/d) in acclimated soils with a 3-percent methane headspace. Degradation of TCE at lesser concentrations (1.3 μM) as the only chloroethene present in fertilized, acclimated soil was much faster (0.12 μmol TCE/L/d) in the presence of 1.2 percent methane. Most of the unsaturated-zone TCE (>99.9 percent) near the contaminant source was sorbed to soil. Results of soil-gas analyses indicate that the concentration of unsaturated-zone TCE near the contaminant source was highest (0.32 μM) in a shallow clay layer, and decreased with depth to the water table. This indicates that the original contamination was mostly from condensed TCE which drained from a degreasing tank to a nearby dry well. The concentration of TCE in unsaturated-zone soil elsewhere throughout the plume increased with depth, indicating that most unsaturated-zone TCE contamination resulted from volatilization losses of TCE from contaminated shallow ground water.

INTRODUCTION

Cometabolism is a non-energy-yielding chemical reaction that occurs fortuitously as a result of microbial metabolic processes (Brock and others, 1984). Cometabolic bioremediation of soil contaminated with chlorinated ethenes is a promising technology that offers the potential for rapid remediation. Cometabolic biotransformation of trichloroethylene (TCE) and cis-1,2-dichloroethylene (cis-DCE), originally described by Wilson and Wilson (1985), typically involves biostimulation of a mixed population of methanotrophs (methane-oxidizing bacteria) to produce methane-monoxygenase enzyme (MMO). This enzyme is synthesized by soil microorganisms to catalyze the reaction of methane to methanol, but can also epoxidize chlorinated ethenes such as TCE, cis-DCE, and vinyl chloride (VC). TCE-epoxide is an unstable compound that rapidly reacts spontaneously to form harmless compounds, such as glycolate and acetate (Roberts and others, 1990).

Picatinny Arsenal, a weapons-development facility in northern New Jersey, is the site of an ongoing study by the U.S. Geological Survey, in cooperation with the U.S. Environmental Protection Agency, of the fate and transport of TCE in an unconfined aquifer. Previous studies at Picatinny Arsenal (Smith and others, 1990; Ehlke, 1988) indicated the presence of elevated concentrations of TCE in unsaturated-zone soil near building 24 as well as the possibility of TCE cometabolic activity. A ground-water-treatment process that came on line in 1992 produces TCE-contaminated gases that require treatment. Development of a cometabolic-based...
treatment system could be used either to treat TCE-contaminated soil gas near building 24 in situ or to process gases containing TCE ex situ.

The major objective of this study was to determine the TCE cometabolic activity of the indigenous microflora in the unsaturated zone at Picatinny Arsenal and to study the effect of a series of amendments on the rate of biotransformation of TCE and cis-DCE. Other study objectives include the quantification of volatile-organic-compound (VOC) contaminant levels in soil gas in the unsaturated zone and concentrations of VOC's sorbed to soil. This report describes TCE and cis-DCE cometabolic activity of the indigenous soil microflora at Picatinny.
Arsenal and methods developed to quantify the mass of unsaturated-zone chlorinated ethenes.

STUDY METHODS

Soil cores were collected at two locations near building 24 (fig. 1) by using a weight-driven 6.98-cm inside-diameter by 60.9-cm-long split-spoon coring device. The apparatus was autoclaved at 121°C for 1 hour prior to transport to the field and was rinsed onsite with sterile, deionized water between successive core samplings. Continuous cores were collected from a depth of 0.6 m to the water table (about 3 m). Soil samples were transferred to 1-qt sterile mason jars, placed on ice, and transported to the laboratory for further processing. After arrival at the laboratory, soil samples were refrigerated at 4 °C prior to analysis for physical properties and sorbed VOC content, as well as for cometabolic activity.

Multilevel soil-gas sampling probes were installed at two locations near building 24 by using one existing soil-gas probe nest previously installed near the overflow pit (dry well) as a model. The probes were constructed from 0.63-cm outside-diameter stainless-steel tubing slotted at the lower end. The probes were installed by augering a 10-cm-diameter borehole to slightly below the static water level, then installing probes at different depths—typically depths of 2.74 m (in water), 2.28 m, 1.37 m, and 0.61 m. The borehole was sealed between successive probes with 0.12 m of bentonite pellets and with 0.15 m of sand above and below the slot openings.

Soil-gas probes were sampled periodically by connecting a short length of tubing to Swagelok fittings on each probe and removing a 1-L or smaller soil-gas sample, which was captured on standard gas-chromatograph (GC) traps for subsequent laboratory gas-chromatographic analysis.

Laboratory assay of GC traps containing soil-gas samples was done by installing a trap containing a soil-gas sample on a Tekmar 4000 purge-and-trap thermal desorber. After testing the trap for gas leaks, GC analysis proceeded by addition of 10 µL of toluene gas in 3 mL of helium to the purge tube as an internal standard, then purging the impinged contents of the GC trap onto the column of a Varian 3600 GC for quantification of volatile hydrocarbons by standard methods (Wershaw and others, 1987).

Ground-water samples were collected from the lowermost soil-gas probe nest by peristaltic pump with a short section (0.3 m) of silicone pump tubing and were stored in amber 40-mL glass vials for subsequent laboratory assay by standard methods (Wershaw and others, 1987). Other water samples from deeper monitoring wells were collected, transported, stored, and analyzed as previously described (Imbrigiotta and others, 1991).

A laboratory study was conducted on unsaturated-zone soil cores to determine TCE and cis-DCE cometabolic activity. The <2-mm size fraction from the 0.6- to 3-m depth was composited and transferred to sterile 100-mL serum vials for determination of TCE and cis-DCE biotransformation activity. The procedure was to transfer 25 g of well-mixed soil to a series of serum vials. Triplicates were used for all treatments. The serum vials were amended with 1 mL of methane or 170 µL of a sterile nutrient (fertilizer) solution (1 g/L each of KH₂PO₄, (NH₄)₂SO₄, and KNO₃) or a methanotroph inoculum to stimulate methanotroph activity. Acclimation of the soil microorganisms to 1-percent methane in the headspace of individual serum vials took 1 to 2 months to reach maximum methanotrophic activity. Peak methanotrophic activity was determined as the point at which methane consumption per unit of time no longer increased. Following acclimation, serum vials were spiked with 1 mL of a concentrated ethene-gas standard, giving an initial headspace concentration of either 1.3 µM TCE or 3.2 µM TCE and 4.3 µM cis-DCE. By using a gas-tight syringe, 600 to 3,000 µL of methane was introduced into certain serum vials, giving a headspace concentration of 0.6 to 3 percent volume-in-volume (v/v) methane. Following introduction of methane and ethenes, 1-mL headspace samples were initially and periodically assayed for methane and ethene concentrations by means of gas chromatography. The results were used to determine the TCE or cis-DCE cometabolic activity of the soil.

MICROBIOLOGY

Soil from site 9A (fig. 2) was studied for biotransformation activity at an initial TCE concentration of 185 µg/L (1.4 µM) in 0.6 percent, 1.2 percent, and 3 percent v/v methane headspace concentrations. The 1.2-percent methane amendment was studied with and without fertilizer. Results (fig. 2) indicate that the greatest TCE removal after 8 days occurred in soil having a 1.2-percent methane...
Figure 2. Biotransformation of gas-phase trichloroethylene in soil samples from core 9A near building 24, Picatinny Arsenal, New Jersey.

Figure 3. Biotransformation of gas-phase trichloroethylene in soil samples from core 9E near building 24, Picatinny Arsenal, New Jersey.
headspace concentration with fertilizer amendment (0.12 μmol TCE/L/d removal). Lesser but significant TCE removal also occurred in 0.6 percent, 1.2 percent (no fertilizer), and 3 percent methane (0.10, 0.07, and 0.06 μmol TCE/L/d removal, respectively). No significant losses of TCE occurred in unacclimated controls over the same period.

Soil from site 9E (fig. 3) also significantly removed TCE and cis-DCE but less rapidly than soil from site 9A, because the initial ethene concentrations studied were higher (nominally 3.2 μM TCE, 4.3 μM cis-DCE) and because TCE and cis-DCE were present as cosubstrates. The results indicate that both TCE and cis-DCE were significantly removed relative to controls over a 28-day period. The greatest TCE removal (0.05 μmol TCE/L/d) occurred in soil amended with 3 percent methane. The least TCE removal (0.037 μmol TCE/L/d) occurred in soil amended with 0.6 percent methane. Cis-DCE likely inhibited TCE biotransformation as a result of competition for the MMO enzyme, as previously reported by Palumbo and others (1991).

Most of the TCE losses in dead controls (0.02 μmol TCE/L/d) are attributed to sorption. Slight biotransformation activity in unacclimated (live) controls (0.03 μmol TCE/L/d, data not shown) is most likely the result of low-level methanotrophic activity, as evidenced by slight production of methane (which stimulates methanotrophs) over the 28-day duration of the experiment. This apparent low-level biotransformation was used to estimate the natural, in situ cometabolic activity at the site. The amendment with a fertilizer solution slightly increased the rate of TCE biotransformation (0.044 μmol TCE/L/d) compared to that in soil amended with 0.6 percent methane (0.037 μmol TCE/L/d); the increase probably would have been greater at a higher methane concentration. Amendment with a methanotrophic inoculum gave much the same result as fertilization with nitrogen and phosphorus.

Cis-DCE was removed much more rapidly than was TCE over 28 days in all treatments containing both compounds (fig. 4) as a result of competitive inhibition for MMO, as has been observed previously (Wackett and others, 1989; Semprini and others, 1990; and Palumbo and others, 1991). The removal of cis-DCE was least in soil amended with 0.6 percent methane (0.056-μmol cis-DCE/L/d removal). Removal of cis-DCE ranged from 0.08 μmol cis-DCE/L/d to 0.09 μmol/L/d in 1.2 percent and 3 percent methane, in soil amended with 0.6 percent methane and fertilizer or in soil amended with 0.6 percent methane, fertilizer, and a methanotrophic inoculum.

![Figure 4](https://example.com/figure4.png)

**Figure 4.** Biotransformation of gas-phase cis-1,2-dichloroethylene in soil samples from core 9E near building 24, Picatinny Arsenal, New Jersey.
SOIL-GAS VOLATILE-ORGANIC-COMPOUND CONCENTRATIONS

Soil-gas TCE concentrations were highest (0.32 μM TCE, or 42.8 μg/L) at a depth of 0.6 m near a former dry well adjacent to building 24 (table 1). A clay layer that is present from 0.6 to 1.2 m is evidently highly contaminated with VOC's and may restrict upward diffusive transport of TCE in unsaturated-zone soil gas. Soil-gas TCE concentrations decreased with depth near building 24 (0.06 μM TCE, 7.7 μg/L at a depth of 2.3 m), indicating that leakage of condensed solvents to the dry well adjacent to building 24 probably was a major contaminant source. Cis-DCE concentrations in soil gas near building 24 also were highest (0.005 μM cis-DCE, 0.5 μg/L) at shallow depths, indicating that significant reductive dehalogenation of TCE occurs in unsaturated-zone soil near building 24.

Concentrations of TCE and cis-DCE in soil gas decreased with distance from the overflow pit near building 24. Generally, the highest TCE and cis-DCE concentrations at sites 9A and 9E, and elsewhere in the plume, were found closest to the water table (table 1).

Table 1. Concentration of trichloroethylene and cis-1,2-dichloroethylene in soil gas near building 24, Picatinny Arsenal, New Jersey

<table>
<thead>
<tr>
<th>Location</th>
<th>Date (d/mo/yr)</th>
<th>TCE concentration (μM)</th>
<th>cis-DCE concentration (μM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9E-V</td>
<td>8/27/92</td>
<td>0.05</td>
<td>0.005</td>
</tr>
<tr>
<td>9E-V</td>
<td>8/27/92</td>
<td>0.10</td>
<td>0.001</td>
</tr>
<tr>
<td>9E-V</td>
<td>12/14/92</td>
<td>0.03</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>9E-V</td>
<td>12/14/92</td>
<td>0.07</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>E2-V</td>
<td>8/27/92</td>
<td>0.32</td>
<td>0.005</td>
</tr>
<tr>
<td>E2-V</td>
<td>8/27/92</td>
<td>0.31</td>
<td>0.003</td>
</tr>
<tr>
<td>E2-V</td>
<td>8/27/92</td>
<td>0.06</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>E2-V</td>
<td>12/14/92</td>
<td>0.03</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>E2-V</td>
<td>12/14/92</td>
<td>0.05</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>9A-V</td>
<td>8/27/92</td>
<td>0.02</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>9A-V</td>
<td>8/27/92</td>
<td>0.02</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>9A-V</td>
<td>12/14/92</td>
<td>0.02</td>
<td>0.003</td>
</tr>
</tbody>
</table>

Table 2. Concentration of trichloroethylene and cis-1,2-dichloroethylene sorbed to unsaturated-zone soil at Picatinny Arsenal, New Jersey

<table>
<thead>
<tr>
<th>Location</th>
<th>Sampling interval (m)</th>
<th>TCE concentration (μg/g)</th>
<th>cis-DCE concentration (μg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9A</td>
<td>0.61-1.22</td>
<td>1.27</td>
<td>0.10</td>
</tr>
<tr>
<td>9A</td>
<td>1.22-1.83</td>
<td>.51</td>
<td>.10</td>
</tr>
<tr>
<td>9A</td>
<td>1.83-2.44</td>
<td>.35</td>
<td>.07</td>
</tr>
<tr>
<td>9A</td>
<td>2.44-3.05</td>
<td>.21</td>
<td>.05</td>
</tr>
<tr>
<td>Dry well</td>
<td>.91-1.00</td>
<td>2.0</td>
<td>nd</td>
</tr>
</tbody>
</table>
CONCLUSIONS

Cometabolic biotransformation of TCE and cis-DCE occurs slowly in situ in unsaturated-zone soils at Picatinny Arsenal and can be increased by acclimation to methane concentrations ranging from 0.6 percent v/v to 3 percent v/v. Fertilizing the soil increased cometabolic biotransformation activity of TCE and cis-DCE.

The fastest TCE removal (0.12 µmol TCE/L/d) occurred in the presence of 1.2 percent methane, with fertilizer amendment, at an initial TCE concentration of 1.3 µM. TCE removal was much slower (0.05 µmol TCE/L/d) when cis-DCE also was present, as a result of competition for the MMO enzyme as well as the concentration of ethenes studied. Bio-transformation of cis-DCE occurred much more rapidly than TCE removal when both ethenes were present (0.09 µmol cis-DCE/L/d and 0.05 µmol TCE/L/d in 3 percent methane, respectively).

The methods developed for quantification of volatile organic compounds in soil gas worked well and could be used effectively elsewhere to measure organic compounds that can be trapped on standard GC traps. Concentrations of TCE in soil gas below an overflow pit near building 24 ranged from 0.03 to 0.32 µM (3.9 to 42.8 µg/L) and were greatest in a clay layer near land surface. Elsewhere throughout the plume, soil-gas TCE concentrations ranged from 0.02 to 0.10 µM (2.6 to 13.3 µg/L) and generally increased with depth to the water table. By far the greatest mass of unsaturated-zone TCE and cis-DCE (more than 99.9 percent) is sorbed to soil from which the ethenes would have to be desorbed prior to cometabolic remediation.

REFERENCES CITED


Desorption of Trichloroethylene From Aquifer Sediments at Picatinny Arsenal, New Jersey

By David Koller¹, Thomas E. Imbrigiotta¹, Arthur L. Baehr¹, and James A. Smith²

Abstract

Desorption of trichloroethylene (TCE) from contaminated aquifer sediments is postulated to be a continuing source of this contaminant to ground water downgradient from the site of a former metal-plating/degreasing operation at Picatinny Arsenal in north-central New Jersey. Flow-through columns were constructed using sediments from four sites within the TCE plume to determine whether TCE desorption was occurring and, if so, at what rate. Results of the column experiments with contaminated sediments indicate that TCE desorption is occurring at all sites tested. Desorption in these columns appeared to occur in two stages—an initial, rapid stage (days to weeks) during which 1 to 10 percent of the total sorbed mass of TCE is released, followed by a slow stage (months to years) during which the remaining 90 to 99 percent is desorbed. Results of a column experiment using sediment artificially contaminated in the laboratory for only 5 days showed the same two-stage desorption, but 65 to 70 percent of the sorbed TCE was desorbed in the initial, rapid stage, and the remaining 30 to 35 percent was desorbed in the slow stage.

A one-dimensional model was developed to determine the desorption rates by simulating the desorption measurements from the column experiments. The model simulates the initial, rapid-stage desorption as an equilibrium process, and simulates the second, slower stage desorption as a kinetic process. Results of model simulations compared well with results of the column experiments. Long-term (slow-stage) rate constants for TCE desorption from Picatinny Arsenal soils calculated by using the model ranged from $0.5 \times 10^{-8}$ to $2.5 \times 10^{-8}$ per second.

INTRODUCTION

From 1973 to 1983, the improperly placed overflow pipe of a metal degreaser released pure-phase TCE into a dry well located in the unsaturated zone in front of Building 24 at Picatinny Arsenal in north-central New Jersey (fig. 1). Leakage of the TCE from the dry well into the underlying unconfined aquifer helped to create a ground-water-contamination plume approximately 500 m long by 250 to 300 m wide at Green Pond Brook, the discharge point of the aquifer (Imbrigiotta and Martin, 1991). Although input of TCE to the ground-water system stopped in 1983, concentrations of TCE in water from wells immediately downgradient from the dry well continue to range from 1,000 to 1,500 µg/L, even after 10 years. This observation implies that a continuing source of TCE exists in the Building 24 area.

One possible explanation is that slow TCE desorption from contaminated aquifer sediments is acting as a persistent source of TCE to the ground water. Solutes may diffuse into intraparticle micropores or dead-end pores of soil particles and become physically inaccessible to the bulk ground water, thereby hindering release of the solutes. Other researchers have noted that the release rates of many low-molecular-weight organic compounds are typically lower than the uptake rates when both are determined in laboratory studies (Szecsody and Bales, 1989;
Figure 1. Location of Building 24 study area at Picatinny Arsenal, New Jersey; areal extent of trichloroethylene plume, October-November 1991; and locations of soil-coring sites and wells sampled.
Di Cesare and Smith (1993) suggest that the slow desorption of organic solutes from soil organic matter may be due to a chemical weathering process in which the arrangement of functional groups of soil humic and fulvic acids is changed by variations in temperature, pH, and ionic strength. The increased tortuosity of the path the solute must travel to be released from the soil organic matter reduces the release rate. In either situation, the assumption of an instantaneous equilibrium between the trapped or adsorbed organic solutes and the bulk ground water is not valid. Additionally, this effect may increase with exposure time of TCE to aquifer sediments (Pavlostathis and Jaglal, 1991; Di Cesare and Smith, 1993). Many studies of desorption rates have been conducted with artificially contaminated sediments and may not accurately reflect long-term desorption rates.

For the purposes of this study, TCE trapped in dead-end or intraparticle pore spaces and TCE partitioned into the soil organic matter are referred to together as "sorbed TCE." Consequently, by this definition "desorbed TCE" includes both TCE that partitions out of soil organic matter and TCE that diffuses from the dead-end or intraparticle pore spaces.

This report describes the results of research to (1) determine whether desorption of TCE from aquifer sediment is a continuing source of TCE to the ground water at Picatinny Arsenal, and (2) estimate the rate of TCE release from field-contaminated sediments. Use of flow-through columns with field-contaminated sediments and artificially contaminated sediments to investigate the desorption phenomenon is described, and a one-dimensional model that simulates the column results and determines the release rate constants is presented.

MATERIALS AND METHODS

Samples of ground water and aquifer sediment were obtained from each of the four sites shown in figure 1. At each site, soil cores were collected within 3 m of an observation well. Soil core samples were collected from 1.5 m above to 1.5 m below the screened interval of the observation well. Ground-water samples were collected from the observation wells shortly before or after the cores were collected.

Soil samples were collected by driving a 7.6-cm by 61-cm split-spoon coring device to the desired depth with a rig-mounted slam bar. The sample was transferred immediately to clean 1-L wide-mouth screw-cap glass bottles. The bottles were filled to minimize headspace, sealed, and stored at 4 °C.

Ground-water samples were collected from the observation well at each coring site according to standard U.S. Geological Survey well-sampling protocols (Wood, 1976; Gibs and Imbrigiotta, 1990). All wells were purged with a 4.4-cm-outside-diameter stainless-steel gear submersible pump. Volatile organic compound (VOC) samples were collected in 40-mL septum-lined screw-capped glass vials and stored at 4 °C.

In the laboratory, three sets of duplicate flow-through column experiments were conducted using sediments from core sites 1, 3, and 5 (fig. 1) as described in detail by Koller (1992). Each column was constructed by transferring a known mass of field-contaminated aquifer sediment to each of the 2.5-cm-inside-diameter by 100-cm-long glass columns. Ground water from the well adjacent to the core site was purged with nitrogen gas to remove VOC's, then used as the feed water for the columns. Sodium azide (200 mg/L) was added to the influent water to inhibit biodegradation of TCE in the columns during the experiments (Pavlostathis and Jaglal, 1991). A low-flow-rate peristaltic pump was used to maintain a steady flow of 0.15 to 0.20 mL/min of the feed water through the columns. Effluent from the columns was sampled several times per day during the first week of an experiment. The sampling frequency was decreased to once daily in the second and third weeks and further decreased to once every 2 or 3 days for the remainder of the experiment. The mass of the water-saturated columns was measured at the end of each experiment to determine the porosity and pore volume of the sediment column.

A fourth column experiment was conducted with sediment that was artificially contaminated with TCE in the laboratory. To prepare this sample, sediment from site 4 was baked at 95 °C for 3 days to remove all sorbed TCE. A portion of the baked sediment was methanol-extracted and checked for complete removal of TCE. The baked sediment was then recontaminated by mixing it with a 40-mg/L aqueous TCE solution for 5 days. The sediment was then separated from the solution and allowed to air dry overnight in a fume hood. Subsamples were analyzed to determine the sorbed TCE concentration. Most of the artificially contaminated sediment was transferred to a set of flow-through columns, and an experiment
identical to those done with the field-contaminated sediment was conducted.

Tracer tests with bromide solution were conducted to determine whether preferred channels of flow existed in the columns. These tests also allowed estimation of dispersion coefficients for use in the model.

Sediment TCE concentrations were determined by using the methanol-extraction procedure described in Koller and others (1996). Concentrations of dissolved TCE in the column effluent samples, in the extract solutions, and in ground-water samples were determined by means of a purge-and-trap/gas chromatographic method described in Kammer and Gibs (1989) and Slator and Ho (1989). The sediment organic-carbon content and particle-size distribution also were measured (Wershaw and others, 1987; Guy, 1969).

DESCRIPTION OF MODEL

A physically based model was developed to test the hypothesis that a fraction of the sorbed TCE is not in equilibrium with or is "less accessible" to the bulk ground-water flowing through the sediment. The fraction of TCE that is in equilibrium is described by the dimensionless equilibrium storage coefficient $s$, which is defined as follows:

$$ s = (\varnothing + K_d \rho (1 - \varnothing)), $$

where $\varnothing$ is porosity (unitless), $\rho$ is bulk sediment density (g/cm$^3$), and $K_d$ is the ratio of sorbed TCE (in grams of TCE per gram of sediment) to the aqueous-phase concentration of TCE (in grams of TCE per cubic centimeter of aqueous phase) at equilibrium. Therefore, the units of $K_d$ are cubic centimeters per gram. The mass-balance equation describing the behavior of the two fractions includes dispersion, advection, and a source term that controls the release of TCE stored in the sediment that is not in equilibrium with the aqueous phase:

$$ \frac{\partial c}{\partial t} = a \frac{\partial^2 c}{\partial x^2} + b \frac{\partial c}{\partial x} + R, $$

where $c$ is the aqueous concentration of TCE (in g/cm$^3$), $t$ is time (in s), $x$ is the length of the soil column (in cm), $a$ is $D/s$, $b$ is $-q/s$, $D$ is the dispersion coefficient (in cm$^2$/s), $q$ is flow rate (in cm/s), and $R$ is rate of TCE mass transfer from sediment not in equilibrium with the aqueous phase (in g/cm$^3$/s). The boundary condition for simulating the column influent is as follows:

$$ c = C_1 at x = 0, $$

where $C_1$ is the influent concentration (in g/cm$^3$).

The other boundary condition is obtained by:

$$ \lim_{x \to \infty} c = C_0, $$

where $C_0$ is the initial column effluent concentration (in g/cm$^3$), which gives the initial condition:

$$ (c = C_0) at t = 0. $$

The release rate $R$ is assumed to be proportional to $M$--the concentration of TCE sorbed to the sediment but not in equilibrium with the aqueous phase (in g/cm$^3$):

$$ R = -\frac{dM}{dt} = kM, $$

where $k$ is the coefficient determining the release rate (in s$^{-1}$). Therefore,

$$ R = kM_0 e^{-kt}, $$

where $M_0$ is the initial total concentration of TCE sorbed to the sediment (in g/cm$^3$), and $M_0 = M$ at $t=0$. Equation (2) subject to the boundary and initial conditions has the following solution, found by Laplace transform:

$$ c = C_0 + w e^{(\alpha x + \beta t)}, $$

where $w = w_1 + w_2 + w_3$, $\alpha = -b/2a$, $\beta = -b^2/4a$, and

$$ w_1 = \frac{C_1 x}{2\sqrt{\pi a}} e^{\beta t} I_1(t) $$

where $c^* = C_1 - C_0$, and

$$ w_2 = \frac{KM_0 x}{2 (\beta + K + a\alpha^2) \sqrt{\pi a}} \left( e^{(\beta + K)} I_2(t) - e^{a\alpha^2 t} I_3(t) \right), $$

$332$
\[ w_3 = \frac{-KM_0 e^{-\alpha x}}{(\beta + K + a\alpha^2)} \left( e^{-(\beta + K)t} - e^{a\alpha^2 t} \right), \quad (11) \]

\[ I_1(t) = \int_0^{t} \frac{\exp \left( \frac{-x^2}{4a\tau} + \beta \tau \right)}{\tau^{3/2}} d\tau, \quad (12) \]

\[ I_2(t) = \int_0^{t} \frac{\exp \left( \frac{-x^2}{4a\tau} + \beta + K \right)\tau}{\tau^{3/2}} d\tau, \quad \text{and} \quad (13) \]

\[ I_3(t) = \int_0^{t} \frac{\exp \left( \frac{-x^2}{4a\tau} + a\alpha^2 \tau \right)}{\tau^{3/2}} d\tau. \quad (14) \]

The solution presented above is similar to that presented by Cameron and Klute (1977) who developed a combined equilibrium-kinetic model and applied it to adsorption of pesticides, nutrients, and metals in soils.

Each column simulation requires the data-input parameters listed in table 1. All input parameters for a given column simulation are measured directly in the experiment or are calculated from measured parameters. The model fits two parameters to simulated data: the fraction of total sorbed TCE in the less accessible phase, \( M/M_0 \), and the constant, \( k \), which describes the rate of release of the less accessible TCE.

**DESORPTION OF TRICHLOROETHYLENE**

**Tracer Tests**

Data collected during bromide-ion tracer tests showed good agreement between the bromide breakthrough times and the predicted breakthrough times based on the gravimetrically determined pore volumes. These findings confirmed that no preferred flow channels existed in the columns. Results of the tracer test also provided estimates of the dispersion coefficient for the flow through the columns for use in simulations of TCE desorption.

**Sediment Characteristics**

The results of physical and chemical analyses of the sediment and ground-water samples are shown in table 2. These results show that all four soil samples were primarily sand with small amounts of silt and clay. In addition, the organic-carbon content of all four samples was low (<0.38 percent). The maximum concentration of TCE in ground water was three orders of magnitude less than the aqueous solubility limit for TCE; therefore, dissolution of pure-phase TCE was unlikely to be a significant alternative source of TCE to the ground water.

**Desorption of Trichloroethylene from Field-Contaminated Sediment**

Results of the three column desorption experiments conducted with field-contaminated sediments are shown in figure 2. Concentrations of TCE remaining on the sediment at any time were normalized by dividing by the initial concentration of TCE sorbed to the sediment. Thus, all curves start at 1.0 and decrease with time as desorption occurs.

In column experiment 1, conducted with the most contaminated sediment collected close to the source (table 1), only 20 percent of the initial sorbed TCE was desorbed after 98 days (98 pore volumes). In column experiment 2, conducted with the moderately contaminated sediment collected farther from the source, 34 percent was desorbed after 110 days (190 pore volumes). In column experiment 3, conducted with the least contaminated sediment collected farthest from the source, 20 percent of the initial sorbed TCE was removed after 78 days (85 pore volumes). Expressed on the basis of percent removal per 100 pore volumes of flow through the columns, removal of initial sorbed TCE concentrations for columns 1, 2, and 3 was 20, 18, and 24 percent, respectively. Thus, desorption in the columns from field-contaminated sediments from the three locations in the plume tested was occurring slowly and at very similar rates. The desorption rate did not seem to depend on the initial sorbed concentration of TCE on the sediment.

Desorption in these columns appeared to occur in two stages—an initial, rapid stage (days to weeks) during which 1 to 10 percent of the total sorbed mass of TCE was released, followed by a slow stage (months to years) during which the remaining 90 to 99 percent was desorbed. A possible explanation for this
Table 1. Summary of column-experiment model-input and -output parameters

[µg/g, micrograms per gram; g, grams; cm², square centimeters; cm, centimeters; g/cm³, grams per cubic centimeters; mL/d, milliliters per day; mL, milliliters; µg/L, micrograms per liter; s, seconds; Field, field-contaminated sediment; Artificial, artificially contaminated sediment; TCE, trichloroethylene; <, less than]

<table>
<thead>
<tr>
<th>Column-experiment number and sediment contamination</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Model-input parameter:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial sorbed TCE concentration (µg/g)</td>
<td>1.7</td>
<td>0.78</td>
<td>0.48</td>
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<tr>
<td>Sediment mass (g)</td>
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<td>688</td>
<td>651</td>
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<tr>
<td>Cross-sectional area (cm²)</td>
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<td>5.07</td>
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<td>Length of soil column (cm)</td>
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<td>100</td>
<td>76.5</td>
<td>89.7</td>
</tr>
<tr>
<td>Initial sorbed TCE concentration (g/cm³)</td>
<td>(M₀)</td>
<td>2.4x10⁻⁶</td>
<td>1.2x10⁻⁶</td>
<td>1.0x10⁻⁶</td>
</tr>
<tr>
<td>Sediment porosity</td>
<td>(θ)</td>
<td>.45</td>
<td>.39</td>
<td>.50</td>
</tr>
<tr>
<td>Sediment density (g/cm³)</td>
<td>(ρ)</td>
<td>2.6</td>
<td>2.5</td>
<td>3.0</td>
</tr>
<tr>
<td>Flow rate (mL/d)</td>
<td>(q)</td>
<td>230</td>
<td>260</td>
<td>245</td>
</tr>
<tr>
<td>Initial TCE concentration in effluent (µg/L)</td>
<td>(C₀)</td>
<td>20</td>
<td>30</td>
<td>12</td>
</tr>
<tr>
<td>Initial TCE concentration in influent (µg/L)</td>
<td>(Cᵢ)</td>
<td>&lt;.2</td>
<td>&lt;.2</td>
<td>&lt;.2</td>
</tr>
<tr>
<td>Pore volume (mL)</td>
<td></td>
<td>230</td>
<td>150</td>
<td>226</td>
</tr>
<tr>
<td><strong>Model-output parameter:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Less accessible fraction of sorbed TCE concentration (M₀/Mₒ)</td>
<td></td>
<td>.99</td>
<td>.90</td>
<td>.90</td>
</tr>
<tr>
<td>Release-rate constant (s⁻¹)</td>
<td>(k)</td>
<td>2.5x10⁻⁸</td>
<td>1.0x10⁻⁸</td>
<td>0.5x10⁻⁸</td>
</tr>
</tbody>
</table>

Table 2. Field data from core sediments and ground water collected for column experiments

[%, percent; µg/L, micrograms per liter; TCE, trichloroethylene; <, less than; well and core-site locations shown in fig. 1]

<table>
<thead>
<tr>
<th>Core- or ground-water-sample characteristic</th>
<th>Column-experiment number</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Core site</td>
<td>1</td>
</tr>
<tr>
<td>Fraction organic carbon (%)</td>
<td>.38</td>
</tr>
<tr>
<td>Sand (%)</td>
<td>92</td>
</tr>
<tr>
<td>Silt + clay (%)</td>
<td>8</td>
</tr>
<tr>
<td>Well sampled</td>
<td>9-H</td>
</tr>
<tr>
<td>TCE concentration in ground water (µg/L)</td>
<td>3,500</td>
</tr>
</tbody>
</table>
Figure 2. Desorption of trichloroethylene from contaminated sediments in four column experiments.
is that the more accessible TCE sorbed to the surface of the sediments is desorbed in the initial, rapid stage, whereas the less accessible TCE that is trapped in dead-end pore spaces or weathered organic matter is desorbed in the second, slower phase.

Desorption of Trichloroethylene from Artificially Contaminated Sediments

Results of the fourth column desorption experiment conducted with artificially contaminated sediments also are shown in figure 2. Desorption of TCE from sediments exposed to contamination for only 5 days proceeded much more quickly than desorption from the field-contaminated sediments. In column experiment 4, 67 percent of the initial sorbed TCE was desorbed after only 54 days (58 pore volumes). All TCE theoretically is desorbed by the time 100 pore volumes flow through this column. Apparently, the elapsed time was insufficient for the TCE to penetrate as many dead-end pore spaces or as much of the organic-material matrix as it did in the field-contaminated sediments. A two-stage desorption curve was observed again; approximately 65 to 70 percent of the sorbed TCE was desorbed in the first, rapid stage, and the remaining 30 to 35 percent was desorbed in the second, slow stage. These findings indicate that TCE-desorption studies conducted with artificially contaminated sediments likely will yield overestimates of field desorption rates.

Simulation of Desorption

Desorption was simulated by using the input-parameter values listed in table 1 for each of the four column experiments. Model-simulated desorption curves were generated and plotted as the solid lines in figure 2. The model simulates a rapid release of the equilibrium-sorbed TCE followed by a relatively slow release of the less accessible TCE. The simulated desorption curves agree fairly well with the measured desorption values over most of each experiment. The model output parameters, M/M₀ and k, also are given for each of the experiments in table 1. The large fractions of less accessible TCE remaining on the sediments at the beginning of the slow desorption stage (90 to 99 percent of initial sorbed TCE) match the estimates made from the measured desorption plots. These results support the hypothesis that removal of sorbed TCE is kinetically limited, and that equilibrium-based models will fail to predict the removal rates because most of the TCE is inaccessible to the water. Mass removal rates for field-contaminated sediments are limited by the low release-rate-constant values controlling the desorption of a large fraction of unavailable sorbed TCE. In contrast, only 33 percent of the sorbed TCE in the artificially contaminated sediment is less accessible, and the removal rate is higher than that for field-contaminated samples. The long-term desorption rate constants calculated with the model ranged from $0.5 \times 10^{-8}$ to $2.5 \times 10^{-8}$ per second.

This model overestimates the removal rate at the end of the desorption experiments, as seen in figure 2. In an updated model the release-rate constant, k, would be a function of the decreasing concentration of TCE on the sediment. The release rate R would be expressed as follows:

$$R = k(M(t)) \times M(t). \quad (15)$$

This change in the expression for R would improve the accuracy of the simulation of the gradual transition between the two desorption stages over that achieved in this study.

SUMMARY AND CONCLUSIONS

Results of laboratory column experiments using aquifer sediments from Picatinny Arsenal in north-central New Jersey indicate that desorption of TCE is occurring and acts as a continuing source of TCE to the plume. Desorption in the columns appeared to occur in two stages—an initial, rapid stage (days to weeks) during which 1 to 10 percent of the total sorbed mass of TCE is released, followed by a slow stage (months to years) during which the remaining 90 to 99 percent is desorbed. Desorption of TCE from field-contaminated sediments is slow compared to desorption of TCE from artificially contaminated sediments. A one-dimensional model was developed to simulate the column desorption data with an initial, rapid-stage desorption as an equilibrium process and a second, slow-stage desorption as a kinetic process. Results of model simulations agreed well with measured column desorption values over time. These results support the hypothesis that most sorbed TCE in the system is in a less accessible fraction (trapped either in dead-end and intraparticle pore spaces or in weathered organic matter) that is not in equilibrium with the ground water and undergoes kinetically limited desorption.
REFERENCES


Effect of Air Drying on Solvent Extraction of Trichloroethylene-Contaminated Soil, Picatinny Arsenal, New Jersey

By David Koller¹, Thomas E. Imbrigiotta¹, and James A. Smith²

Abstract

The effect of air drying trichloroethylene (TCE)-contaminated soils prior to extraction with methanol to determine the concentrations of sorbed TCE was investigated. Saturated-aquifer soil and ground-water samples were collected at five locations within a TCE plume in ground water at Picatinny Arsenal, New Jersey. Each soil sample was split into two fractions: one fraction underwent extraction while wet and the other underwent extraction after being air dried overnight. Concentrations of TCE in the wet soils were corrected for TCE in the soil moisture by subtracting the TCE concentrations determined in the ground-water samples. Comparison of the extraction results for air-dried and wet soils showed that, for four of the five samples, the concentration of sorbed TCE in the air-dried fraction was higher than or not significantly different from that in the wet fraction. In addition, the precision of the extraction results for air-dried soils was not significantly different from the extraction results for wet soils.

INTRODUCTION

Study of the fate and transport of volatile organic compounds (VOC's) in ground water and the unsaturated zone requires analytical methods to determine the mass of contaminants sorbed to soil. Present standard techniques for analyzing soil containing VOC's involve concentration of the contaminants by extracting them into an organic solvent or by gas-purging them from the soil samples onto a solid adsorbent (Sawhney and others, 1988; U.S. Environmental Protection Agency, 1986). The VOC's in the resulting extracts can then be separated and quantified with a gas chromatograph and a suitable detector. One important limitation of these analytical procedures is that neither procedure can accurately quantify the mass of VOC's sorbed only to the soil. Because the above-described concentration procedures are routinely applied to the soil sample without drying, they yield the combined masses of VOC's sorbed to the soil and VOC's dissolved in the water in the saturated soil sample. For soil samples with low organic-carbon content that are exposed to ground water containing high concentrations of VOC's, the mass of VOC's in the soil water may be of comparable magnitude to the mass sorbed to the soil. For these cases, analysis of the whole-soil sample—that is, soil and water—will result in an overestimation of the mass of VOC's sorbed to the soil.

Recently, several researchers have reported that VOC's sorbed to natural soil that has been exposed to contamination for long periods are resistant to desorption into both water and air (Steinberg and others, 1987; Sawhney and others, 1988; Smith and others, 1990; Koller, 1992). If these findings are correct, it is possible that certain soil samples could be air-dried prior to extraction and analysis. Air drying of the soil would effectively remove the VOC's in the soil water by volatilization and leave only the fraction of the VOC's that is truly sorbed to the soil sample. Although repartitioning of volatilizing VOC's back onto the soil is possible, this process is minimized if the air drying is performed in a setting where the

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²Department of Civil Engineering and Applied Mechanics, University of Virginia, Charlottesville, VA
vapors are constantly being removed, such as a fume hood. Direct determination of the concentration of VOC's sorbed to air-dried soils would avoid potential errors involved in analyzing wet soils and groundwater samples and correcting for the TCE content of the soil moisture. Air drying also would simplify the handling of soil samples, because precautionary measures to prevent the volatilization of the VOC's would not be necessary. This paper describes the results of a study to determine whether overnight air drying of contaminated soil significantly reduces the concentration of sorbed TCE.

DESCRIPTION OF THE FIELD SITE

Picatinny Arsenal, in north-central New Jersey, has been the site of an interdisciplinary research study of the fate and transport of chlorinated solvents in groundwater by the U.S. Geological Survey (USGS) since 1986. Ground-water contamination by TCE downgradient from Building 24, site of a former metal plating/degreasing operation, is well-documented (Imbrigiotta and Martin, 1991; Imbrigiotta and others, 1991; Sargent and others, 1990). From 1973-83, TCE vapors from a degreasing unit condensed in an overflow pipe and discharged to a dry well in front of the building (fig. 1). Discharge of TCE from the dry well into the aquifer has created a plume of ground-water contamination that extends 500 m downgradient from Building 24 to Green Pond Brook, the point of ground-water discharge from the system. Contamination from Building 24 has remained primarily in the 15- to 18 m-thick unconfined sand and gravel aquifer. The hydrogeology and environmental processes affecting the fate and transport of chlorinated solvents in the ground water at this site have been discussed in detail by Imbrigiotta and Martin (1991), Ehlke and others (1991), Martin (1991), Wilson and others (1991), and Smith and others (1990).

MATERIALS AND METHODS

Samples of ground water and aquifer material were collected from the TCE-contaminated part of the aquifer at each of the five sites shown in figure 1. At each site, soil cores were collected within 3 m of an observation well. Soil-core samples were collected from 1.5 m above to 1.5 m below the screened interval of the observation well. Ground-water samples were collected from the observation wells shortly before or after the cores were collected.

Soil samples were collected by driving a 7.6-cm by 61-cm split-spoon coring device to the desired depth with a rig-mounted slam bar. The sample was transferred quickly to clean 1-L wide-mouth screw-cap glass bottles. The bottles were filled to minimize headspace, sealed tightly, and stored at 4 °C until analysis.

Ground-water samples were collected from the observation well at each coring site according to standard USGS well-sampling protocols (Wood, 1976; Gibs and Imbrigiotta, 1991). All wells were purged with a 4.4-cm o.d. stainless-steel, gear submersible pump. VOC samples were collected in 40-mL septum-lined screw-capped glass vials and stored at 4 °C until analysis.

In the laboratory, soil samples were removed from the sealed bottles and immediately passed through a 2-mm sieve. Sieving homogenized the sample and resulted in a more uniform soil for extraction. The wet, sieved soil sample was then divided into four subsamples. The first three subsamples were analyzed for organic-carbon content, moisture content, and particle-size distribution (Wershaw and others, 1987; Fishman and Friedman, 1985; Guy, 1969). The fourth subsample was used to quantify the concentration of TCE sorbed to the soil. One-half of this wet subsample was extracted and analyzed immediately by using the procedure described below, whereas the other half was air-dried for 24 hr at 23 °C in a fume hood and then subjected to the same extraction and analytical procedure.

TCE was extracted from all soil samples by a slight modification of the procedure described in Sawhney and others (1988) and Smith and others (1990). From 10 to 15 g of soil were measured into preweighed 50-mL glass serum vials. Chromatography-grade methanol (approximately 50 mL) was weighed into each vial until the headspace comprised less than 5 percent of the vial volume. Vials were capped with aluminum-foil liners, Teflon-lined septa, and aluminum crimp caps. The vials were shaken thoroughly by hand and placed in an oven at 75 °C. The small headspace in each vial accommodated expansion of the methanol during heating. After 24 hours, each vial was shaken again and returned to the oven. After a total of 48 hours, the vials were removed and allowed to cool. Each vial contained a settled soil layer and a clear methanol layer.
EXPLANATION

Shaded area between lines represents the area where trichloroethylene concentrations are greater than 10 micrograms per liter.

--- 10 --- LINE OF EQUAL CONCENTRATION OF TRICHLOROETHYLENE—Concentration in micrograms per liter. Dashed where approximately located.

Site 5  41–9 Soil-coring site, sampled well, and identifiers.

Figure 1. Location of Building 24 study area at Picatinny Arsenal, New Jersey; areal extent of trichloroethylene plume, October-November 1991, and locations of soil-coring sites and wells sampled.
Subsamples of the methanol supernatant were analyzed for TCE by using a purge-and-trap/gas-chromatography (PT/GC) method. The gas chromatograph used was equipped with a wide-bore capillary column and a photoionization detector and a Hall electrolytic conductivity detector in series. This analytical procedure is a modification of that described by Kammer and Gibbs (1989) and Slator and Ho (1989). The chromatographic data were collected and processed by using a personal computer with data-reduction software. Standards in the range of TCE concentrations in the samples were run each day. Ground-water samples were analyzed by the same PT/GC method.

The detection limit for TCE in water or extract samples was 0.2 μg/L. On the basis of the maximum dilution factor, the average volume of methanol used in each extraction, and the average mass of soil extracted, the detection limit for TCE sorbed to the soil was about 15 μg/kg.

Quality-control procedures to ensure reliable and accurate results included the following: (1) Selected soil samples were subjected to a second 48-hour extraction to determine whether all the TCE had been removed during the first extraction. (2) For each set of extractions, two to four vials containing methanol with known TCE concentrations underwent the same extraction procedure to determine whether losses due to sorption to the glass vial or volatilization through the cap occurred. (3) All soil samples were extracted at least in triplicate; several soil samples were extracted up to 10 times. (4) Replicate analyses of individual extract solutions and ground-water samples were performed frequently.

The concentrations of TCE sorbed on air-dried soils were calculated on the basis of the mass of TCE determined in the methanol extract and the dry weight of the soil extracted. The mass of TCE determined in the methanol extract for wet soils was corrected (decreased) by the mass of TCE contained in the soil moisture (based on the results of the analysis of the ground-water samples). Depending on the sample, this correction ranged from 3 to 53 percent of the methanol-extracted TCE mass. In addition, the weight of the wet soil was corrected by subtracting the mass attributable to soil moisture.

**RESULTS OF SOIL-EXTRACTION ANALYSES**

The results of physical and chemical analyses of the ground-water and soil samples (other than the extraction analyses) are shown in table 1. All five soil samples were primarily sand with small amounts of silt and clay. In addition, the organic-carbon content of all five samples was low (<0.38 percent). Soil-moisture contents ranged from 12 to 24 percent. TCE concentrations in ground water differed by two orders of magnitude among the five sites.

Results of sequential extractions on three different soil samples showed that 95 to 99 percent of the TCE present in the soil samples was recovered during the first 48-hour extraction and little more TCE was recovered by extracting for an additional 48 hours. All subsequent soil extractions were, therefore, 48-hour extractions.

The results of the extraction of methanol samples spiked with known TCE concentrations showed that an average of 95 percent of the spiked amount was recovered. This finding indicates that the amount of TCE lost by sorption to the glass vial or volatilization through the cap was insignificant and did not affect the accuracy of the procedure. In addition, methanol blanks and soil samples containing no TCE that underwent the extraction process showed no detectable TCE concentrations when analyzed, indicating that no cross-contamination occurred during the extraction and analysis procedures.

The results of the extractions of the air-dried and wet soils are shown in table 2. In four of the five samples tested, the concentrations of TCE extracted from the air-dried soils were essentially equal to or greater than the concentrations of TCE extracted from the wet soils. A two-tailed t test was applied to the five sets of analysis results to determine whether the means were significantly different at the 95-percent confidence level (Zar, 1974). The t-test results, shown in the last column of table 2, confirm that no significant difference in mean sorbed TCE concentrations exists between air-dried and wet soils from sites 1, 2, and 4.

At site 5, the concentration of TCE on the air-dried soils was significantly higher than that on the wet soils, possibly because some of the aqueous TCE may have volatilized before the soil could be sealed in the extraction vessel. Therefore, the apparent total concentration of TCE in the extraction vessel would have been lower than the actual value. Consequently,
the apparent concentration of sorbed TCE after subtracting the correction for the actual concentration of TCE in the soil water (1,900 µg/L) also would have been lower than the actual value. Concentrations of TCE sorbed on wet soil samples from highly contaminated sites may be overadjusted downward as a result of this phenomenon.

Overadjustment does not occur for soil samples from sites where TCE concentrations in ground water are low because the TCE contribution from the soil water is negligible. At site 2, for example, the correction for the low TCE concentration in ground water makes almost no difference in the calculated concentration of sorbed TCE (3 percent), because the

Table 1. Physical and chemical characteristics of aquifer soils and ground water at five sites at Picatinny Arsenal, New Jersey

<table>
<thead>
<tr>
<th>Site</th>
<th>Soil-sample depth (m)</th>
<th>Soil-moisture content (%)</th>
<th>Soil particle size distribution (%)</th>
<th>Organic-carbon content (%)</th>
<th>Obs.-well name</th>
<th>Depth of screened interval (m)</th>
<th>TCE conc. (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.0 - 7.6</td>
<td>24</td>
<td>Sand 92</td>
<td>0.38</td>
<td>9-H</td>
<td>4.6-6.1</td>
<td>3,500</td>
</tr>
<tr>
<td>2</td>
<td>2.7 - 8.8</td>
<td>15</td>
<td>Sand 100</td>
<td>.16</td>
<td>9-A</td>
<td>3.0-7.3</td>
<td>70</td>
</tr>
<tr>
<td>3</td>
<td>2.7 - 7.3</td>
<td>14</td>
<td>Sand 96</td>
<td>.17</td>
<td>9-E</td>
<td>4.3-5.8</td>
<td>1,300</td>
</tr>
<tr>
<td>4</td>
<td>6.4 -11.0</td>
<td>12</td>
<td>Sand 94</td>
<td>.03</td>
<td>92-5</td>
<td>7.9-9.4</td>
<td>220</td>
</tr>
<tr>
<td>5</td>
<td>3.4 - 7.9</td>
<td>14</td>
<td>Sand 99</td>
<td>.22</td>
<td>41-9</td>
<td>4.9-6.4</td>
<td>1,900</td>
</tr>
</tbody>
</table>

Table 2. Concentrations of sorbed trichloroethylene on air-dried and wet soils sampled at Picatinny Arsenal, New Jersey

<table>
<thead>
<tr>
<th>Site</th>
<th>Soil-moisture condition</th>
<th>Number of replicate samples</th>
<th>Sorbed TCE conc. (µg/kg)</th>
<th>Std. dev.</th>
<th>CV (%)</th>
<th>Sig. diff. @ p=0.05</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>air-dried</td>
<td>4</td>
<td>2,600</td>
<td>900</td>
<td>35</td>
<td>NSD</td>
</tr>
<tr>
<td></td>
<td>wet</td>
<td>4</td>
<td>2,600</td>
<td>400</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>air-dried</td>
<td>10</td>
<td>420</td>
<td>29</td>
<td>7</td>
<td>NSD</td>
</tr>
<tr>
<td></td>
<td>wet</td>
<td>10</td>
<td>410</td>
<td>95</td>
<td>23</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>air-dried</td>
<td>9</td>
<td>700</td>
<td>150</td>
<td>22</td>
<td>SD</td>
</tr>
<tr>
<td></td>
<td>wet</td>
<td>8</td>
<td>900</td>
<td>60</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>air-dried</td>
<td>7</td>
<td>25</td>
<td>6</td>
<td>22</td>
<td>NSD</td>
</tr>
<tr>
<td></td>
<td>wet</td>
<td>5</td>
<td>27</td>
<td>9</td>
<td>34</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>air-dried</td>
<td>9</td>
<td>460</td>
<td>41</td>
<td>9</td>
<td>SD</td>
</tr>
<tr>
<td></td>
<td>wet</td>
<td>8</td>
<td>330</td>
<td>110</td>
<td>34</td>
<td></td>
</tr>
</tbody>
</table>

The precision of the air-dried-sample analyses was better than the precision of the wet-sample analyses for three of the five soil samples tested. The overall coefficient of variation (standard deviation/mean) of the five air-dried-sample analyses was 19 percent and of the five wet-sample analyses was 23 percent. A t test comparing these means showed no significant difference between the coefficients of variation for air-dried samples and wet samples at the 95-percent confidence level.
One possible reason that TCE does not desorb when field contaminated soil samples are air-dried is that the TCE may be physically trapped in dead-end pore spaces or in the intraparticle pore spaces of the aquifer materials. In this case, the TCE may not be able to diffuse readily to the surface of the soil to volatilize.

Another possible explanation is that the TCE is held on the soil by a nonequilibrium, kinetically limited desorption mechanism. Koller (1992) measured field TCE soil/water partition coefficients (Koc’s) at Picatinny Arsenal and found a strong disequilibrium in favor of the soils—that is, the concentrations of TCE on the soils are much higher than would be predicted if an equilibrium with the ground-water TCE concentrations is assumed. Smith and others (1990) previously found an analogous disequilibrium for TCE in the unsaturated zone, with much higher concentrations of TCE on the soils than would be predicted from the soil-gas TCE concentrations. In addition, Koller (1992) determined, by means of column experiments with aquifer sediments from Picatinny Arsenal, that TCE desorbs much more slowly from soils that have been contaminated for a long time (years) than from similar soils that have been artificially contaminated for a short time (days). The kinetic limitation may result from a weathering process that changes the arrangement or composition of the soil organic matter over long periods. Di Cesare and Smith (1993) have proposed that functional groups of soil humic and fulvic acids may reconfigure and rearrange over time in response to changes in temperature, pH, and ionic strength of the ground water. When desorption begins, the rate of solute diffusion from the soil organic matter may be much less than the original rate of diffusion into the soil because the tortuosity of the path the solute must travel has increased greatly over the period of contamination. This hindered desorption of TCE from the organic phase may help prevent the loss of TCE by volatilization during air drying.

SUMMARY AND CONCLUSIONS

The data presented here show that overnight air drying of aquifer soils that have been contaminated for long periods does not result in a significant loss of TCE from most samples. The overall precision of the extraction results was not significantly different for air-dried sediments than for wet sediments. Because there appears to be little difference in the accuracy or precision of air-dried and wet-soil extractions, and because air drying soils simplifies sample handling in the field and laboratory, air drying of TCE-contaminated soil samples at Picatinny Arsenal prior to extraction is deemed acceptable and advantageous. In addition, analysis of air-dried soil samples avoids potential errors analyzing wet-soil samples, which must be corrected for the TCE content of the soil water. Though caution must always be used in applying the findings from one site to another, the results of these analyses of samples from Picatinny Arsenal probably have transfer value to many other sites at which the geology and duration of TCE contamination are similar.

The extraction procedure described here yields accurate and reproducible results for soil with TCE concentrations greater than 15 μg/kg. This technique has the advantage of requiring no special instrumentation other than the PT/GC setup ordinarily used for the analysis of VOC’s in water.

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In Situ Biotransformation of Trichloroethylene and cis-1,2-dichloroethylene at Picatinny Arsenal, New Jersey

By Theodore A. Ehlke, Barbara H. Wilson, John T. Wilson, and Thomas E. Imbrigiotta

Abstract

Biotransformation of trichloroethylene (TCE) and cis-1,2-dichloroethylene (cis-DCE) was estimated within a part of the unconfined aquifer at Picatinny Arsenal, New Jersey, that is contaminated with chlorinated solvents. The first-order in situ biotransformation rate for TCE was estimated to range from about 0.001 to 0.05 per week. The in situ removal rates generally are more rapid than the biotransformation rates that were previously measured in the laboratory in soil cores collected at the arsenal.

In situ biotransformation was estimated to occur more slowly for cis-DCE than TCE. The first-order biotransformation rate for cis-DCE ranged from about 0.01 to 0.03 per week. Long-term concentrations of TCE and cis-DCE in ground water at one location indicate that TCE concentration probably was not the major determining factor limiting the transformation of TCE to cis-DCE in ground water.

INTRODUCTION

Picatinny Arsenal, a weapons-development facility in northern New Jersey, is the site of an ongoing U.S. Geological Survey (USGS) study of the fate and transport of chlorinated solvents in an unconfined aquifer. The primary sources of TCE to the unconfined aquifer near building 24 were two unlined wastewater lagoons behind the building and an overflow pit in front of the building that received TCE waste from a vapor degreaser from 1960 to 1983 (Sargent and others, 1990). The TCE plume in the unconfined aquifer extends about 540 m from building 24 to Green Pond Brook, the local ground-water discharge area (fig. 1). Ground water in the aquifer contained an estimated 970 kg of TCE in 1991 (Mary Martin, U.S. Geological Survey, oral commun., 1993).

The major mechanisms for removal of chlorinated ethenes from ground water in the unconfined aquifer are reductive dehalogenation by soil microorganisms, volatilization from contaminated ground water to the unsaturated zone, sorption to aquifer material, and advective transport toward Green Pond Brook. Estimates of volatilization, sorption, and advective-transport at the arsenal are described elsewhere (Smith and others, 1990; Martin, 1991; Voronin, 1991; and Koller, 1992) and were estimated to be significantly less than losses of ethenes from ground water as a result of reductive dehalogenation. Cometabolic biotransformation of TCE and cis-DCE, although probably important in the unsaturated zone, is likely a minor removal mechanism in the saturated zone because concentrations of oxygen and methane are low there (Ehlke and Imbrigiotta, 1996).

Reductive dechlorination (dehalogenation) is the process by which a chlorine atom is replaced by a hydrogen atom under anaerobic conditions, forming cis-DCE. Cis-DCE is similarly dechlorinated, forming vinyl chloride (VC), a potent carcinogen. The electron-transfer mechanism producing reductive dehalogenation in situ has not been well described, but has been shown elsewhere to be largely microbially mediated (Freedman and Gossett, 1989; Sewell and Gibson, 1991).

Reductive dechlorination of TCE and cis-DCE at Picatinny Arsenal has been described in a series of reports (Wilson, 1989; Ehlke and others, 1991; Wilson and others, 1991). Rates of dechlorination of TCE in the laboratory with soil cores collected from several sites within the unconfined aquifer at the arsenal
ranged from <0.008 to 0.02 per week (Wilson and others, 1991). Results of field studies at the arsenal indicate that rates of reductive dechlorination of TCE and cis-DCE (as estimated from appearance of end products and disappearance of reactants in ground water) vary spatially in the unconfined aquifer (Imbrigiotta and others, 1991). This report describes estimated in situ reductive-dechlorination rates for TCE and cis-DCE at different sites within the unconfined aquifer, variation in the biotransformation rate over time, and differences between laboratory and field estimates of dechlorination rates.
METHODS

In situ removal rates of TCE and cis-DCE were estimated from concentrations of TCE and cis-DCE in samples of ground water from a series of wells along the path of ground-water flow within the contaminant plume (fig. 1) by using estimates of advective transport of TCE and cis-DCE (Martin, 1991; Voronin, 1991). Gains and losses of TCE and cis-DCE in ground water due to nonbiological (physical) mechanisms, such as sorption, desorption, dispersion, and volatilization, were considered to be small in comparison to those due to dechlorination. Because physical losses of TCE and cis-DCE from ground water, particularly at the boundaries of the contaminant plume, may not be insignificant everywhere, the in situ rates of TCE and cis-DCE dechlorination (computed as removal rates, but implied to be largely biologically mediated) reported in this paper may be overestimated. Desorption of TCE from contaminated soils, primarily near building 24, has been the major mechanism by which TCE is released to ground water at Picatinny Arsenal since its use there ceased in 1983. Desorption and sorption mechanisms were assumed to be constant over the time interval for advective flow of TCE between successive downgradient wells. Results of a previous study (Koller, 1992) indicate that this assumption probably is reasonable. The presence of nonaqueous-phase liquid (NAPL) TCE in the aquifer near the former overflow pit has not been verified in soil-core samples, but is indicated by modeling results (Mary Martin, U.S. Geological Survey, oral commun., 1993). If NAPL TCE were present at Picatinny Arsenal, the rate of solution of TCE probably would be relatively constant and probably would not affect biotransformation (removal) computations. Losses of TCE by dispersion and volatilization mechanisms were considered to be insignificant at the scale of the plume for the purposes of removal-rate computation. TCE flux to and from the unsaturated zone is relatively constant and is estimated to be minor (Cho and others, 1993). The time-of-travel for ground water between building 24 and Green Pond Brook is about 2.1 years, at an average velocity of 0.7 m/d (Martin, 1991).

The rate of microbial removal of TCE and cis-DCE between downgradient wells within the plume was estimated by means of a first-order equation that includes concentrations of TCE and cis-DCE in ground-water samples collected at various times and the estimated advective-transport rate. The computation incorporates the assumption that a particle of water intercepted by an upgradient well is transported advectively to the downgradient well, and that the possible nonbiological losses of TCE and cis-DCE described previously are insignificant. The rate of removal was computed as follows:

$$K_d = \frac{L}{T_w} \ln \left( \frac{C_1}{C_2} \right),$$

where

- $K_d$ is the estimated in situ removal rate (per week);
- $C_1$ is the upgradient concentration of chlorinated ethene;
- $C_2$ is the downgradient concentration of chlorinated ethene at a later time (date when upgradient well was sampled, plus $T_w$);
- $T_w$ is the advective transport time, in weeks, between up- and down-gradient wells; and
- $L$ is the natural logarithm.

Change in the rate of removal of TCE at one well (9A; fig. 2) over the time interval from 1982 to 1992 was estimated by using geochemical data collected by non-USGS personnel during 1982-87 and by USGS personnel during 1987-92. The former results are listed in Sargent and others (1990).

ESTIMATE OF THE RATE OF IN SITU REMOVAL OF TRICHLOROETHYLENE AND CIS-1,2-DICHLOROETHYLENE

Removal of TCE and cis-DCE was estimated along a transect parallel to ground-water flow within the contaminated part of the unconfined aquifer (fig. 1) by using a first-order reaction (eq. 1). Most transport of chlorinated ethenes in ground water near the contaminant source occurs in the shallow flow system (3.5-11 m depth). Results of particle-tracking analysis indicate that concentrations of ethenes in ground water at wells 9B, 9E, CAF-2, and 92-5 (fig. 1) provide a reasonably good estimate of local ground-water quality in the shallow flow regime (Voronin, 1991). Advective flow between these wells varies from about 75 days (wells 9B-9E) to 180 days (wells 9E-CAF-2). Advective flow in the deeper part of the unconfined aquifer (depth greater than 12 m) is an important transport mechanism for ethenes in ground water near Green Pond Brook. For additional details of flow in the unconfined aquifer, see Voronin (1991).

Removal of ethenes in the deeper part of the unconfined aquifer was estimated for that part of the aquifer between wells 92-3 and 112-7 (fig. 1). This location corresponds to ground-water flow 15 to 16.8 m deep in permeable layer 2, as described by Voronin
Figure 2. Concentration of trichloroethylene, cis-1,2-dichloroethylene and vinyl chloride at well 9A, Picatinny Arsenal, N.J., 1982-92.
Ground-water flow in this system is slightly slower than flow at shallower depths (about 0.5 m/d between wells 92-3 and 112-7 compared to 0.7 m/d in the shallower part of the unconfined aquifer between wells CAF-2 and 92-5). The increase in contact time per unit of distance increases the removal rate of ethenes in the deeper aquifer.

The *in situ* removal of TCE in shallow ground water near the contamination source (between wells 9B and 9E) ranges from <0.001 to 0.08 per week (median 0.02 per week) on the basis of concentrations of ethenes in ground water collected at different times corresponding to the estimated ground-water-flow time between these wells. Most of the removal is attributed to anaerobic biotransformation processes for the reasons previously stated.

Removal of TCE from ground water in the shallow flow system between wells 9E and CAF-2 is more rapid than removal nearer the contamination source (median 0.05 per week, range 0.02-0.08 per week). This difference is attributed to increased biological activity associated with biotransformation of fuel oil. A plume of degradation products of fuel oil near building 31 partly overlaps the TCE plume in this part of the study area (fig. 1). A leaking diesel-fuel tank was removed from near building 31 in 1986. This tank was a likely source of hydrocarbons, which could be metabolized by methanogens to form methane and other products, such as fatty acids and reduced nonvolatile organic compounds that have been reported to be indirectly associated with *in situ* biotransformation of chlorinated ethenes. Major and others (1991) reported that *in situ* anaerobic biotransformation of organic solvents (largely methanol) enhanced the dechlorination of tetrachloroethylene (PCE) and TCE.

Results of analyses of ground-water samples collected at a well upgradient from the fuel-oil spill (well 13-2) and two wells downgradient from the spill (wells 34-1 and 111-1) (table 1) indicate greater-than-background concentrations of methane, ammonia, dissolved organic carbon, and certain minor elements (such as iron and manganese) in wells 34-1 and 111-1 compared to concentrations of these constituents at the uncontaminated well (13-2). The redox potential and concentrations of dissolved oxygen and nitrate were lower in wells 34-1 and 111-1 than in well 13-2. *In situ* biotransformation of TCE and cis-DCE in the unconfined aquifer near wells 34-1 and 111-1 probably is rapid, as indicated by the relatively high ratio of the concentration of products of TCE biotransformation (cis-DCE and VC) to the reactant concentration. For example, the ratio of TCE:cis-DCE concentrations at well 34-1 was 1.5:1, and the ratio of TCE:VC concentrations at well 111-1 was 2:1 (table 1). By comparison, the TCE cis-DCE concentration ratio at well 92-3, which is near a part of the unconfined aquifer in which biotransformation of TCE is slow, ranged from 90:1 to 140:1 during the same period.

Removal of TCE in the part of the unconfined aquifer between wells CAF-2 and 92-5 is very slow, ranging from <0.001 to 0.001 per week (median 0.001 per week). The low concentrations of cis-DCE and VC observed at the downgradient well (92-5) (from <1 µg/L to 10 µg/L cis-DCE, and <1 µg/L VC) indicate that biotransformation of TCE and cis-DCE there probably is significantly slower than biotransformation closer to the contamination source. Analyses of soil samples collected at location CAF-2 during a previous study indicated very slow biotransformation of TCE (<0.01 per week) (Wilson and others, 1991).

Removal of TCE from ground water in a deeper part of the unconfined aquifer (12-16.8 m deep) was estimated from concentrations of TCE and cis-DCE in ground water in wells 92-3 and 112-7. In general, results indicate that removal of TCE is fairly rapid

### Table 1. Results of water-quality analyses of ground-water samples from Picatinny Arsenal, New Jersey [mg/L, milligrams per liter; N, nitrogen; µg/L, micrograms per liter; <, less than]

<table>
<thead>
<tr>
<th>Constituent or characteristic</th>
<th>13-2</th>
<th>34-1</th>
<th>111-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Redox potential, millivolts</td>
<td>209</td>
<td>160</td>
<td>34</td>
</tr>
<tr>
<td>Oxygen, dissolved, mg/L</td>
<td>4.3</td>
<td>.4</td>
<td>.2</td>
</tr>
<tr>
<td>Ammonia, dissolved as N (mg/L)</td>
<td>.01</td>
<td>.02</td>
<td>.45</td>
</tr>
<tr>
<td>Nitrate, dissolved as N (mg/L)</td>
<td>1.9</td>
<td>.2</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Iron, dissolved, µg/L</td>
<td>10</td>
<td>20</td>
<td>2,300</td>
</tr>
<tr>
<td>Manganese, dissolved, µg/L</td>
<td>10</td>
<td>42</td>
<td>210</td>
</tr>
<tr>
<td>Organic carbon, dissolved, mg/L</td>
<td>.7</td>
<td>1.2</td>
<td>4.2</td>
</tr>
<tr>
<td>Methane, µg/L</td>
<td>1**</td>
<td>77*</td>
<td>325</td>
</tr>
<tr>
<td>Trichloroethylene, µg/L</td>
<td>4</td>
<td>15</td>
<td>16</td>
</tr>
<tr>
<td>cis-1,2-Dichloroethylene, µg/L</td>
<td>&lt;1</td>
<td>10</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Vinyl chloride, µg/L</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>8</td>
</tr>
</tbody>
</table>

*Samples were collected in December 1989, June 1989.
**Samples were collected in April 1990.
(median 0.025 per week) in this part of the aquifer. The presence of modest concentrations of daughter products of TCE biotransformation at well 112-7 (22-120 µg/L cis-DCE and 3-4 µg/L VC) indicate that biotransformation of TCE probably is much more rapid at the 14 to 15.7 m depth of well 112-7 than at shallower depths in this area. In comparison, the concentration of cis-DCE at well 112-8 (same location as well 112-7 but screened at 4.8 to 6.4 m instead of 14.0 to 15.7 m) ranged from <1 to 7 µg/L over the same period.

Cis-DCE removal occurred more slowly in the unconfined aquifer than did removal of TCE. Removal of cis-DCE in a shallow part of the aquifer between wells 9A and 111-1 ranged from 0.01 to 0.03 per week. Removal of cis-DCE in the deeper part of the aquifer between wells 92-3 and 112-7 was estimated to range from about 0.001 to 0.01 per week. This finding is consistent with results reported elsewhere, which indicate that the rate of cis-DCE biotransformation to VC is slower than the rate of production of cis-DCE from TCE (Barrio-Lage and others, 1986). Similar rates for the biotransformation of cis-DCE (0.01-0.06 per week) were reported by Barrio-Lage and others (1986) for Florida Everglades muck. The observed concentrations of TCE, cis-DCE, and VC in ground water at Picatinny Arsenal also strongly indicate that the in situ removal rate of cis-DCE (largely by biotransformation) is less than that for TCE.

VARIATION IN BIOTRANSFORMATION RATE WITH TIME

Variation in the rate of biotransformation of TCE to cis-DCE during 1982-92 was estimated from results of analyses of ground-water samples collected at well 9A. Time-series plots of the reactant (TCE) and the intermediate product of biotransformation (cis-DCE) are shown in figure 2. The plot indicates that, although the concentration of TCE in ground water decreased from about 300 µg/L in 1982 to 66 µg/L in 1992, the concentration of cis-DCE in ground water increased slightly from about 43 µg/L in 1982 to 79 µg/L in 1992. The biotransformation of TCE to VC is shown in equation 2. If the overall biotransformation rate described by the following series of reactions was limited by the concentration of the first reactant (TCE), the formation of cis-DCE would be expected to decrease as the concentration of TCE decreased

\[
\begin{align*}
H & \quad Cl \\
\text{C} = \text{C} & \quad + e^- \\
\text{Cl} & \quad \text{Cl} \\
\text{C} = \text{C} & \quad + Cl^- \\
\text{Cl} & \quad \text{Cl} \\
\text{H} & \quad \text{Cl} \\
\text{H} & \quad \text{Cl} \\
\text{C} & \quad \text{C} & \quad + Cl^-. (2)
\end{align*}
\]

However, the rate of formation of cis-DCE during 1982-92 was nearly constant. The reaction rates of TCE to cis-DCE and from cis-DCE to VC are more likely to depend on the concentration of other constituents (electron donors), that have not yet been identified at Picatinny Arsenal. These results also provide field evidence that the in situ biotransformation of cis-DCE to VC occurs more slowly than the formation of cis-DCE from TCE. If the biotransformation of cis-DCE to VC occurred more rapidly than the formation of cis-DCE, the in situ pooling of cis-DCE at certain points in the unconfined aquifer would not be observed. DiStefano and others (1992) have hypothesized that electrons transferred during methanogenesis may be involved in reductive dechlorination of PCE and TCE.

COMPARISON OF FIELD-AND LABORATORY-MEASURED BIOTRANSFORMATION RATES

Anaerobic biotransformation rates of TCE and cis-DCE, which were estimated previously in a series of laboratory batch experiments (Ehlke and others, 1991; Wilson and others, 1991), generally indicated similar or lower biotransformation rates than were estimated from field results (table 2). The laboratory estimate of the rate of TCE biotransformation ranged from <0.01 to 0.02 per week within the contaminant plume, compared to field estimates of the rate of TCE biotransformation at Picatinny Arsenal, which range from 0.001 to 0.05 per week. The reasons for these differences are unclear at this time but may reflect experimental conditions in the laboratory, including the inability to reproduce in situ concentrations of reduced electron donors, which are required for the reductive dehalogenation process to proceed. Also, observed in situ removal of TCE and cis-DCE includes losses from dispersion, volatilization, and advective transport--processes that were not included in laboratory removal estimates.
Table 2. Laboratory and field estimates of trichloroethylene biotransformation in the unconfined aquifer at Picatinny Arsenal, New Jersey

<table>
<thead>
<tr>
<th>Location and sample type</th>
<th>Biotransformation rate, per week</th>
<th>Ground-water velocity between locations shown in fig. 1 (m/d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9H to 9F, GW</td>
<td>&lt;0.001 0.08, median 0.02 (field)</td>
<td>0.3</td>
</tr>
<tr>
<td>9B, soil</td>
<td>0.02 (laboratory)</td>
<td></td>
</tr>
<tr>
<td>9E to CAF-2, GW</td>
<td>0.02 0.08, median 0.05 (field)</td>
<td>0.6</td>
</tr>
<tr>
<td>CAF-2, soil</td>
<td>&lt;0.01 (laboratory)</td>
<td></td>
</tr>
<tr>
<td>CAF-2 to 92-5, GW</td>
<td>&lt;0.001 0.001, median 0.001 (field)</td>
<td>0.7</td>
</tr>
<tr>
<td>92-5, soil</td>
<td>0.012 (laboratory)</td>
<td></td>
</tr>
<tr>
<td>92-3 to 112-7, GW</td>
<td>0.025 (field)</td>
<td>0.5</td>
</tr>
<tr>
<td>112-7, soil</td>
<td>0.008 (laboratory)</td>
<td></td>
</tr>
<tr>
<td>41-9, soil</td>
<td>0.004 (laboratory)</td>
<td></td>
</tr>
</tbody>
</table>

SUMMARY AND CONCLUSION

Rates of biotransformation of TCE and cis-DCE within the contaminated part of the unconfined aquifer at Picatinny Arsenal, N.J., were estimated. Rate constants for anaerobic biotransformation of TCE in situ were estimated to range from about 0.001 to 0.05 per week in different parts of the unconfined aquifer. In situ biotransformation of TCE generally is estimated to occur more rapidly than was previously measured in laboratory studies with soil cores from the arsenal. The rate of in situ biotransformation of cis-DCE is slower than the rate of biotransformation of TCE, ranging from about 0.01 to 0.03 per week. These estimates are within the range of reported rates of biotransformation of TCE and cis-DCE in soil at other locations. Concentrations of TCE and cis-DCE in ground water during 1982-92 indicate that the TCE concentration is not a limiting factor in determining the rate of biotransformation of TCE to cis-DCE.

REFERENCES


Surfactant-Enhanced Remediation of Ground Water at Picatinny Arsenal, New Jersey

By James J. Deitsch and James A. Smith

Abstract

The efficiency of pump-and-treat remedial systems is limited by the slow, kinetic mass transfer of organic contaminants from soil to water. The scope of this research is to determine whether the addition of the nonionic surfactant, Triton X-100, to the aqueous phase can artificially increase the rate of trichloroethene (TCE) mass transfer from soil to water at Picatinny Arsenal. The rate of TCE mass transfer (desorption) from soil to water is modeled as the product of a mass-transfer coefficient and a concentration gradient. Laboratory experiments were conducted using continuous-flow stirred tank reactors (CFSTR's), with and without Triton X-100, to study the effect of the surfactant on the rate of desorption of TCE from soil to water. Preliminary results indicate that the rate of desorption is increased by the presence of Triton X-100 in the aqueous phase. Two possible mechanisms are responsible for the increased desorption rate: First, the addition of Triton X-100 above its critical micelle concentration can increase the apparent water solubility of TCE and thus increase the concentration gradient between the sorbed and aqueous phases. Second, Triton X-100 can increase the mass-transfer coefficient. Future experiments are planned to determine the precise mechanism affecting the rate of desorption.

INTRODUCTION

Picatinny Arsenal is located in a northeast-southwest trending valley in Morris County, New Jersey. During 1960-81, Building 24 (fig.1) was the site of metal-plating and degreasing operations that used trichloroethene (TCE) as the degreasing solvent. Wastewater from these operations was discharged into an overflow dry well and two unlined lagoons adjacent to Building 24. As a result of these activities, the unconfined, sand-and-gravel aquifer beneath the site is contaminated with TCE. The plume of ground-water contamination is indicated in figure 1. Details of the site's hydrogeology and history of ground-water contamination have been given by Imbrigiotta and others (1996).

Remediation of TCE-contaminated ground water at Picatinny Arsenal was begun in September 1992 with the implementation of a pump-and-treat system. The system employs five withdrawal wells which extract ground water from the subsurface at a combined rate of approximately 150 gal/min. TCE is removed from the extracted water by two air-stripping towers and an activated carbon filter. The water is then returned to Green Pond Brook. The locations of the withdrawal wells are shown in figure 1.

Pump-and-treat remediation is a commonly used technology for the remediation of contaminated ground-water systems. However, the overall effectiveness of the technology is limited by the slow, kinetic mass transfer of organic contaminants from soil to water (Smith and others, 1991; Pavlostathis and Mathavan, 1992; Di Cesare and Smith, 1993). The removal of contaminated ground water and subsequent replacement with upgradient water induces a contaminant-concentration gradient between the sorbed and aqueous phases. The concentration gradient causes the sorbed organic contaminants to desorb slowly from the soil organic matter and
Trichloroethene concentrations greater than 10 micrograms per liter. October-November 1991

Soil sampling location

Figure 1. Map of study area showing building 24, region of trichloroethene concentrations greater than 10 micrograms per liter, remedial withdrawal wells, and the soil sampling location.

contaminate the inflowing ground water. Therefore, pump-and-treat remedial systems may have to operate for tens of years before a large fraction of the total subsurface contamination is removed.

This paper presents preliminary data that will be used to determine whether the rate of TCE mass transfer from soil to water at Picatinny Arsenal can be artificially increased by the addition of a nonionic surfactant, Triton X-100, to the aqueous phase.

MATERIALS AND METHODS

The soil sample used in this study was collected from Picatinny Arsenal from a composite depth of 3 to 6 ft at the location indicated in figure 1. The organic-carbon content of the sample is 31 percent. 500 μCi of [14C] TCE (specific activity equal to 6.2 mCi/mmol) was obtained and mixed with nonradioactive TCE to yield a net volume of 6 mL pure liquid. The resultant chemical and radiochemical purity of the radioisotope was greater than 98 percent.

In preparation for the experiment, the soil was air dried in a fumehood for 24 hours and then heated for 4 hours at 105°C. These precautions were taken to reduce the presence of TCE on the soil. The trace amounts of TCE remaining on the soil do not affect the results of the experiment. After heating, the soil was passed through a #10 sieve (2-mm opening) to insure that the soil subsamples would be homogeneous.

The kinetic desorption of TCE from soil to water was studied using a continuous-flow stirred tank reactor (CFSTR) that consisted of a glass column with an inside diameter of 1.0 cm and a length of 15 cm. The nominal volume was approximately 12 cm³. A Teflon O-ring shield provided a leak-free seal and a chemically inert surface. The bed supports were also Teflon and had 20 μm openings. All surfaces inside the CFSTR were either glass or Teflon. Each CFSTR contained approximately 5 g of soil.

The inflow and outflow junctions of each CFSTR were prepared identically. 5-cm lengths of Teflon tubing were connected to the inflow and outflow ports of the CFSTR. The thread adapters, nuts, and ferrules formed an airtight seal. The opposite ends of the Teflon tubes were connected to separate two-way Teflon valves. A 1-m length of silicone rubber tubing was attached to the inflow valve. The outflow valve was connected to a 30-cm length of Teflon tubing. After all the hydraulic junctions of the system were sealed, 10 mL of distilled water was poured into the CFSTR and the end fitting was closed.

The CFSTR was fastened to a rotary shaker. The inflow tubing was run through a peristaltic pump, and the end of the tube was immersed in a reservoir of distilled water containing 200 mg/L sodium azide. The addition of sodium azide eliminates any microbiological activity in the CFSTR (Pavlostathis and Mathavan, 1992). The CFSTR was then shaken at 150 revolutions per minute (rpm) continuously to insure a completely mixed system. Distilled water was pumped through the CFSTR at a rate of 12 mL/hr for 3 days. This procedure was followed for three reasons: First, air bubbles in the CFSTR were removed, thus limiting the potential for volatilization after TCE is injected. Second, small amounts of soil exit the CFSTR during early flow periods. After the third day, little or no additional soil exits the CFSTR. Thus, the mass of soil in the CFSTR remains constant after 3 days, allowing the exact mass to be calculated. Third, the 3-day flow period insures that the system is
flowing at a constant rate before injecting the TCE. A total of six CFSTR's were prepared in this manner.

After 3 days, the pumping was discontinued and the valves closed. The thread adapters at the effluent ports were removed. A 25 μL syringe was used to inject a known volume of the [14C]-labeled TCE solution into each of the six CFSTR's. The thread adapters were then replaced. The CFSTR's were continuously shaken at 150 rpm for 1 week. At the end of the equilibration period, the CFSTR's were prepared for sampling.

The CFSTR's were separated into two groups of three. A solution of distilled water and 200 mg/L sodium azide was the reservoir for group one. The second group used a solution of distilled water, 200 mg/L sodium azide, and 300 mg/L Triton X-100 surfactant. The critical micelle concentration (CMC) of Triton X-100 is 140 mg/L (Kile and Chiou, 1989). The two solutions were pumped through the columns at flow rates of approximately 2 mL/hr. (One column flowed at 6 mL/hr because of an equipment problem).

Approximately 0.5 mL of effluent from the CFSTR's was collected periodically in 7-mL scintillation vials. The exact amount of effluent captured was determined gravimetrically. The radioactivity of the samples was measured with a Packard Tri-Carb 1900CA liquid-scintillation analyzer, and the corresponding TCE concentrations were calculated with a standard curve relating concentration to counts per minute. During periods when no samples were collected, the effluent was collected in glass tubes to quantify the flow rate. The sampling was conducted for 7 days.

A CFSTR was prepared with no soil to verify that no loss of TCE occurred during the sampling period, and to verify that the system was completely mixed. A known volume of [C14]-labeled TCE was injected and allowed to equilibrate for 1 week. The CFSTR was then sampled continuously for 8 hours using the described procedure.

**BACKGROUND THEORY**

The governing equation for the conservation of mass for the aqueous phase in the CFSTR, assuming a completely mixed system, is as follows:

$$V_w \frac{dC}{dt} = Q(C_{in} - C) + r_a V_w,$$

where $V_w$ is the volume of water in the reactor (in mL), $Q$ is the flow rate through the CFSTR (in mL/hr), $C_{in}$ is the inflow solute concentration (in mg/L), $C$ is the aqueous phase concentration throughout the reactor (in mg/L), $r_a$ is the reaction term (in mg/Lhours ), and $dC/dt$ is the time rate of change of the solute concentration. In this study, TCE is the solute being modeled and desorption is assumed to be the only reaction component.

The desorption of TCE is represented by a first-order kinetic mass-transfer relation. This relation can be expressed mathematically as

$$\frac{dC_s}{dt} = -K(C_s - K_d C),$$

where $C_s$ is the sorbed solute concentration (in mg/g), $K$ is the mass-transfer coefficient (in hr$^{-1}$), $K_d$ is the partition coefficient (L/g), and $dC_s/dt$ is the mass of solute desorbed per gram of soil per hour (in mg/gxhours). The rate of desorption is directly proportional to $K$ and the chemical potential gradient between the sorbed and aqueous phases.

Equation 2 can be multiplied by $M_s$, the mass of soil in the CFSTR (g), and divided by $V_w$. The resulting equation is substituted into equation 1 to account for the desorption of TCE. When $C_{in}$ is zero, as in the experiments reported in this paper, the following equation results:

$$\frac{dC}{dt} = -\frac{Q C}{V_w} + \frac{M_s}{V_w} K (C_s - K_d C)$$

where all terms have been described previously. Equation 3 can be solved analytically when desorption is not present, yielding

$$C = C_0 e^{\left(\frac{Q}{V_w}\right)},$$

where $C_0$ is the initial concentration (in mg/L). Equation 4 quantifies the effluent TCE concentration from the CFSTR with no soil. The effluent concentrations obtained from this experiment are compared to concentrations generated by equation 4 in the Results section of this paper.

A fourth-order Runge-Kutta method was used to numerically solve equation 3 with desorption present. The only unknown in the system of equations is $K$. By finding a functional form of $K$ to fit the experimental data, the value of $K$ was quantified for each CFSTR. The resulting values of $K$ were compared to determine whether the presence of the surfactant affected the rate of desorption.
RESULTS

The decline of aqueous TCE concentrations over a period of 8 hr for the CFSTR with no soil present is shown in figure 2. According to equation 4, the decrease of aqueous TCE concentrations follows an exponential decline if the flow rate and volume are constant. Both conditions were met. The TCE concentrations observed by sampling the CFSTR matched the TCE concentrations generated by the analytical solution. In fact, an exponential regression analysis of the data provided a correlation coefficient, r, of -0.9799. Based on the strong correlation, two important conclusions are drawn. First, the assumption of a completely mixed reactor is justified by the experimental results. Second, because the observed TCE concentrations do not lie below the curve produced by equation 4, the sampling procedure appears to retain all of the TCE in the sample effluent.

The numerically fitted aqueous TCE concentration curves for the six CFSTR's with soil are shown in figure 3. The independent variable is the number of pore volumes that have flowed through the CFSTR's. The number of pore volumes is defined as the overall volume of flow divided by the volume of water in the reactor, $V_W$. In this report, $V_W$ is 10 mL. The use of pore volumes facilitates the comparison of CFSTR's with different flow rates. The accuracy of the numerical solutions in describing the data of two

CFSTR's is shown in figure 4. The numerical solutions applied to the remaining four CFSTR's also closely matched the laboratory data. The TCE concentrations shown in figure 3 rapidly decline in all six CFSTR's during the first five pore volumes. However, the rate of decline of TCE concentrations in the CFSTR's with Triton X-100 decreases after five pore volumes. In contrast, the rapid rate of decline in the three CFSTR's without Triton X-100 continues until 10 pore volumes. After 10 pore volumes, the rate of decline of the TCE concentrations is slightly higher for Triton X-100 CFSTR's. This continues until 40 pore volumes, where the six curves become essentially identical.

The relation shown by the TCE concentration curves in figure 3 is directly related to the rate of desorption in the six CFSTR's. According to equation 3, the rate of decrease of the aqueous TCE concentrations is a function of dilution and the rate of desorption; dilution increases the rate of decrease, whereas, desorption decreases the rate of decrease. Because dilution is standardized for all six CFSTR's by using the number of pore volumes as the independent variable, the deviations in figure 3 are caused by differences in desorption rates. Because the TCE concentrations are nearly identical for the first five pore volumes, the rates of desorption in the six CFSTR's are similar in this time interval. However, after five pore volumes, the rate of desorption in the
CFSTR's with Triton X-100 is greater than in the CFSTR's without Triton X-100. This accounts for the higher observed TCE concentrations in the CFSTR's with Triton X-100 than in the CFSTR's without Triton X-100. Triton X-100 increases the rate of TCE desorption from the soil to water relative to results of experiments without Triton X-100, as shown in figure 3.

The curves generated in figure 3 use a time-varying mass-transfer coefficient. The experimental data could not be described adequately with a constant mass-transfer coefficient. A scheme using two different constant values also was investigated but proved to be unsuccessful. The results of this study indicate that the rate of desorption varies with time.

Finally, the mass fraction of TCE removed from the soil phase as a function of pore volumes of flow for the six CFSTR's is shown in figure 5. Using 35 pore volumes as a reference point, the mass fractions of TCE desorbed from the soil by the CFSTR's with Triton X-100 are 0.64, 0.72, and 0.72. In comparison, the fraction of TCE desorbed from the soil by the CFSTR's without Triton X-100 after 35 pore volumes of flow are 0.41, 0.54, and 0.58. On average, the CFSTR's with Triton X-100 removed 18.33 percent more TCE after 35 pore volumes than did the CFSTR's without Triton X-100. It should be noted that even though the equilibration time of this experiment was just 1 week, only 51 percent of the TCE on average was desorbed from the soil in the CFSTR's without Triton X-100 after 35 pore volumes. The desorption of TCE from soil to water is kinetically limited even for short equilibration periods.

**DISCUSSION**

Two possible mechanisms are responsible for the higher desorption rate in CFSTR's containing Triton X-100 relative to the rate in CFSTR's without Triton X-100. The first mechanism is well documented (Kile and Chiou, 1989; Kile and Chiou, 1990); the addition of a surfactant above its CMC can increase a solute's apparent water solubility. By increasing a solute's apparent water solubility, the sorption coefficient ($K_d$) of the compound is decreased. Analysis of equation 2 shows that, as $K_d$ decreases, the concentration gradient between the sorbed and aqueous phases increases, therefore increasing the rate of desorption.

Second, the addition of Triton X-100 to the CFSTR may increase the mass-transfer coefficient, $K$. The addition of Triton X-100 to the water decreases surface tension. A decrease in surface tension allows the water to fill and swell the organic polymer matrix.
to a greater extent than under normal surface tensions. By swelling the organic matrix, it is possible that diffusive paths which previously were not passable are now open as pathways for the TCE to desorb.

In the analysis of the previous results, $K_d$ was assumed to remain constant in both systems. The differences in desorption rate were assumed to be the result of an alteration of the mass-transfer coefficient. At this point, the effect of Triton X-100 on the $K_d$ of TCE has not been quantified. However, future experiments are planned to investigate the effects of the surfactant on $K_d$. Once the relation between $K_d$ and surfactant concentration is determined, the mechanism responsible for the increased desorption rate can be identified.

Other planned experiments include determination of the effect of residence time on the desorption of TCE using Triton X-100. The 1-week equilibration period for this study clearly shows a kinetic effect on the rate of desorption. It is expected that equilibration times longer than 1 week will show stronger kinetic effects. By performing experiments with equilibration times longer than 1-week, the effectiveness of Triton X-100 and other surfactants on long-term contaminated soils can be evaluated.

**SUMMARY**

Preliminary experimental results indicate that the addition of the nonionic surfactant Triton X-100 is effective in artificially increasing the rate of TCE mass transfer from the soil to the aqueous phase. Two mechanisms are potentially responsible: First, the mass-transfer coefficient could have been increased by the addition of Triton X-100. Second, the concentration gradient could have been increased by a reduction of $K_d$ because of the presence of Triton X-100. The precise mechanism for this increased desorption rate is still under study.

**REFERENCES**


Sampling Borehole Flow to Quantify Aquifer Cross-Contamination by Volatile Organic Compounds

By Ronald A. Sloto

Abstract

A combination of borehole geophysical methods, measurements of vertical borehole flow, and analyses of borehole-fluid samples were used to assess the extent of aquifer cross-contamination in the Stockton Formation in Hatboro, Pennsylvania. The Stockton consists of interbedded nonmarine sandstone and siltstone-mudstone. Most industrial, public-supply, and monitoring wells drilled into the Stockton Formation are constructed as open holes with short casings and are open to multiple water-bearing zones. Caliper, fluid-resistivity, fluid-temperature, natural-gamma, and single-point-resistance logs were run in 19 boreholes 149 to 656 feet deep to locate water-bearing fractures and determine zones of vertical borehole-fluid movement. The direction and rate of vertical borehole-fluid movement was measured by injecting a slug of high-conductance fluid at a specific depth in the borehole and monitoring the movement of the slug with the fluid-resistivity tool. After intervals of borehole flow were determined, samples of moving fluid were extracted from nine boreholes at a rate less than that of the measured borehole flow and analyzed for volatile organic compounds. An estimated 80.9 kilograms per year of volatile organic compounds were moving downward through the sampled boreholes from the contaminated, upper part of the aquifer to the lower part, which is tapped by public-supply wells. Trichloroethylene accounts for 94 percent and 1,1,1-trichloroethane accounts for 3 percent of the compounds.

INTRODUCTION

Many public supply, industrial, and monitoring wells in the United States are completed as open holes that obtain water from several formations or from several water-bearing zones in a single formation. The advantage to this construction practice is that a much greater yield can be obtained than if a well is open to a single formation or water-bearing zone. The disadvantage is that these boreholes, which connect several aquifers or water-bearing zones, commonly short circuit the ground-water-flow system and act as conduits for the transport of contaminants. The existence and magnitude of this problem is largely undetermined.

This paper presents some of the results of a study done by the U.S. Geological Survey (USGS) in cooperation with the U.S. Environmental Protection Agency (USEPA) to identify and assess cross-contamination by abandoned multiaquifer boreholes. A combination of borehole geophysical methods, measurements of vertical borehole flow, and analyses of borehole-fluid samples were used to assess the extent of aquifer cross-contamination in the Stockton Formation in Hatboro, Pa. The purpose of this paper is to show how those techniques were used to identify and determine the magnitude of cross-contamination.

Location and Description of Study Area

The study area is part of Hatboro Borough in Montgomery County, Pa. (fig. 1). It is centered around an older industrial area typical of many other communities in southeastern Pennsylvania. Much of the industry dates back to or prior to the World War II era. Industrial and public-supply wells drilled into the Stockton Formation were constructed as open holes with short casings and are open to multiple water-bearing zones. Downward fluid movement in
EXPLANATION

- 1236 BOREHOLE AND IDENTIFICATION NUMBER (Prefix MG omitted from number)
- 1221 MONITORING WELL CLUSTER AND IDENTIFICATION NUMBER (Prefix MG omitted from number)

Figure 1. Location of boreholes and monitoring-well clusters.
boreholes in the Stockton Formation was identified using borehole geophysical methods in the township north of Hatboro (Sloto and Davis, 1983).

The study area includes the Raymark site, which has been designated as an National Priorities List (NPL) site by the USEPA (fig. 1). The Raymark NPL site has been the location of a metal fabrication shop since 1948. Solvent containing trichloroethylene (TCE) was used in the manufacturing process to clean and degrease metal parts. Over several decades of operation, TCE was introduced into the environment at the location of a solvent storage tank, a metal degreaser, and four disposal lagoons. Other industrial facilities in the vicinity, which included manufacturers of kitchen ranges, toys, television picture tubes, and metal parts, also used solvents in their manufacturing processes.

Geological Setting

Hatboro is underlain by the Upper Triassic Stockton Formation. The Stockton is the basal unit in the Triassic-Jurassic Newark basin, which contains 16,000 to 20,000 ft of nonmarine sedimentary rocks of the Newark Supergroup. Following deposition, the sediments were tilted, faulted, uplifted, and eroded. The Stockton Formation is about 6,000 ft thick and includes alluvial fan deposits, fluvial and lacustrine sandstones, and fluvial and near-shore lacustrine mudstones and siltstones (Turner-Peterson and Smoot, 1985). Thick, poorly defined upward fining cycles possibly were deposited by large, perennial, meandering rivers. One of the characteristics of the Stockton is thick-bedded to locally massive arkosic sandstones.

In the Hatboro area, the Stockton Formation strikes approximately N. 65° E. and dips approximately 9° NW. The rocks are chiefly interbedded arkosic sandstone and siltstone-mudstone. Grain size changes both laterally and vertically. The rocks that underlie the study area belong to the middle arkose member (Rima and others, 1962), but boreholes may penetrate the underlying lower arkose member.

Hydrological Setting

The rocks of the Stockton Formation form a complex, heterogeneous, multiaquifer system. This aquifer system is comprised of a series of gently dipping sandstone and siltstone-mudstone beds that form lithologic units, a few inches to tens of feet thick; each lithologic unit has different hydraulic properties. Secondary permeability is dominant. In general, the sandstone beds are the principle water-bearing units, but some of the finer-grained beds may contain water-bearing zones. Because of the softness and fine grain size of the siltstone-mudstone beds, water-bearing openings tend to clog. In addition, the soft siltstone-mudstone beds deform without breaking under stress. Harder sandstone beds tend to develop joints and are more permeable.

All of the lithologic units are hydraulically connected. Ground water in units at or near the land surface is under unconfined conditions; ground water in the deeper units may be confined or semiconfined. Most deep boreholes penetrate several water-bearing zones and are multiaquifer boreholes. Each water-bearing zone usually has a different hydraulic head. The hydraulic head in a deep borehole is the composite head of the several water-bearing zones it penetrates. In boreholes penetrating several water-bearing zones, borehole fluid will flow in the direction of lower head. Water-level measurements made at the MG-1222 borehole cluster on August 5, 1991, showed a water level 36.48 ft below land surface for the open interval 33 to 63 ft below land surface, a water level 49.91 ft below land surface for the open interval 118 to 138 ft, and a water level 55.85 ft below land surface for the open interval 185 to 195 ft. Water moves downward through the aquifer in response to this downward head gradient, which is caused in part by the pumping of deep public supply wells.

MEASUREMENT OF BOREHOLE FLOW

Caliper, fluid-resistivity, fluid-temperature, natural-gamma, and single-point-resistance logs were run in 19 boreholes (fig. 1) 149 to 656 ft deep to interpret lithostratigraphy, locate water-bearing fractures, and determine zones of vertical borehole-fluid movement. A complete suite of geophysical logs from MG-1222, the deepest borehole in a three-borehole cluster, is shown on figure 2. Construction of a threedimensional lithostratigraphic model for the study area using caliper, natural-gamma, and single-point-resistance logs was described by Sloto and others (1992).

Correlation of caliper logs with single-point-resistance, fluid-resistance, and fluid-temperature logs was used to identify fractures and water-producing and water-receiving zones. Caliper logs were used to identify fractures and possible water-bearing openings. Not all fractures shown on the caliper log of borehole MG-1222 (fig. 2), for example, are water-bearing fractures. Single-point-resistance logs were sometimes helpful for identification of water-bearing zones.
Figure 2. Caliper, natural-gamma, single-point resistance, fluid-temperature, and fluid-resistivity logs from borehole MG-1222.
Fluid-resistivity and fluid-temperature logs were used to identify water-producing and water-receiving zones and to determine intervals of vertical borehole flow. Water-producing and water-receiving zones were identified by sharp changes in resistivity. Intervals of borehole flow were identified by a low resistivity gradient between water-producing and water-receiving zones. The fluid resistivity log from borehole MG-1222 (fig. 2) shows sharp changes in fluid resistivity at 83, 128, and 189 feet below land surface, indicating water-producing or water-receiving zones. Fluid-temperature logs from wells with no borehole flow generally show a decrease in fluid temperature with depth in the upper part of the borehole and an increase in fluid temperature with depth as a function of the geothermal gradient in the lower part of the borehole. Intervals of vertical borehole flow were identified by little or no temperature gradient. Intervals of nearly constant temperature in borehole MG-1222 (fig. 2) at depths of 50 to 80, 80 to 130, and 130 to 192 ft below land surface indicate intervals of borehole flow.

Upon completion of geophysical logging, the suite of logs was evaluated to choose zones of potential borehole flow. The direction and rate of vertical borehole-fluid movement was then determined by injecting a slug of high-conductance fluid at a specific depth in the borehole and monitoring the movement of the slug with the fluid-resistivity tool. This is the brine-tracing method described by Patten and Bennett (1962). The lower limit of flow measurement is about 0.5 gal/min in a 6-in.-diameter borehole. Borehole flow was calculated by:

\[ Q = 7.481 \times V \pi r^2, \]  

where \( Q \) is borehole flow, in gallons per minute; 
\( V \) is the rate of vertical borehole fluid movement, in feet per minute; and 
\( r \) is the radius of the borehole, in feet.

For borehole MG-1222, slugs of high-conductance fluid were injected at 85, 95, 120, and 175 ft below land surface. Downward flow at the rate of 2.3, 2.6, 2.8, and 3.4 gal/min, respectively, was measured. Figure 3 shows the movement of the slug of high-conductance fluid injected 175 ft below land surface. The slug moved downward at 2.3 ft/min, which corresponds to a flow rate of 3.4 gal/min. High-conductance-fluid slugs were injected at different depths in 18 boreholes to determine the direction and rate of vertical borehole flow. As many as eight slugs were injected in a single borehole. Fluid movement at rates up to 14 gal/min was measured (table 1). The predominant direction of fluid movement was downward. Downward borehole flow was measured in 15 boreholes. Generally, fluid moves downward from fractures in both the siltstone-mudstone beds and sandstone beds in the upper part of the aquifer, which is unconfined, to fractures in the sandstone beds in the lower part of the aquifer, which is semiconfined or confined. Both upward and downward flow was measured in borehole MG-220; flow was downward in the upper part of the borehole and upward in the lower part of the borehole. No measurable flow was detected in boreholes MG-487 and MG-488, which are about 50 ft apart. The direction and rate of borehole flow was not determinable for borehole MG-212 because of the large diameter (14 in.), rough borehole wall, and possible horizontal flow through the formation.

**Figure 3.** Movement of a high-conductance fluid slug injected 175 feet below land surface in borehole MG-1222.

**SAMPLING BOREHOLE FLOW**

After intervals of borehole flow were determined, a sample of the moving fluid was extracted with a nitrogen-driven bladder pump at a rate less than that of the measured borehole flow. Samples were collected from nine boreholes (MG-220, 951, 1236, 1237, 1238, 1239, 1240, 1241, and 1242; see fig. 1) and analyzed for volatile organic compounds (VOCs) by the USGS National Water-Quality Laboratory in Arvada, Colo. None of the boreholes sampled were on the Raymark NPL site. For boreholes with downward flow, these samples represent water moving from the shallow to the deeper part of the aquifer.
### Table 1. Borehole-flow measurements

<table>
<thead>
<tr>
<th>Borehole Identification number</th>
<th>Logged depth (feet)</th>
<th>Purpose for which borehole was drilled</th>
<th>Direction of borehole flow</th>
<th>Maximum measured flow (gallons per minute)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MG-212</td>
<td>244</td>
<td>Public supply</td>
<td>Not determinable</td>
<td>Not determinable</td>
</tr>
<tr>
<td>MG-220</td>
<td>470</td>
<td>Public supply</td>
<td>Down and up</td>
<td>4.1 (Down)</td>
</tr>
<tr>
<td>MG-295</td>
<td>656</td>
<td>Industrial supply</td>
<td>Down</td>
<td>3.0</td>
</tr>
<tr>
<td>MG-487</td>
<td>510</td>
<td>Industrial supply</td>
<td>None</td>
<td>0</td>
</tr>
<tr>
<td>MG-488</td>
<td>186</td>
<td>Industrial supply</td>
<td>None</td>
<td>0</td>
</tr>
<tr>
<td>MG-951</td>
<td>323</td>
<td>Public supply</td>
<td>Down</td>
<td>2.0</td>
</tr>
<tr>
<td>MG-1114</td>
<td>149</td>
<td>Monitoring</td>
<td>Down</td>
<td>5.7</td>
</tr>
<tr>
<td>MG-1221</td>
<td>195</td>
<td>Monitoring</td>
<td>Down</td>
<td>4.3</td>
</tr>
<tr>
<td>MG-1222</td>
<td>200</td>
<td>Monitoring</td>
<td>Down</td>
<td>3.4</td>
</tr>
<tr>
<td>MG-1223</td>
<td>196</td>
<td>Monitoring</td>
<td>Not measured</td>
<td>Not measured</td>
</tr>
<tr>
<td>MG-1235</td>
<td>143</td>
<td>Monitoring</td>
<td>Down</td>
<td>&lt;.5</td>
</tr>
<tr>
<td>MG-1236</td>
<td>122</td>
<td>Monitoring</td>
<td>Down</td>
<td>14</td>
</tr>
<tr>
<td>MG-1237</td>
<td>169</td>
<td>Monitoring</td>
<td>Down</td>
<td>1.6</td>
</tr>
<tr>
<td>MG-1238</td>
<td>200</td>
<td>Monitoring</td>
<td>Down</td>
<td>.9</td>
</tr>
<tr>
<td>MG-1239</td>
<td>166</td>
<td>Monitoring</td>
<td>Down</td>
<td>.7</td>
</tr>
<tr>
<td>MG-1240</td>
<td>159</td>
<td>Monitoring</td>
<td>Down</td>
<td>.7</td>
</tr>
<tr>
<td>MG-1241</td>
<td>174</td>
<td>Monitoring</td>
<td>Down</td>
<td>1.5</td>
</tr>
<tr>
<td>MG-1242</td>
<td>178</td>
<td>Monitoring</td>
<td>Down</td>
<td>.7</td>
</tr>
<tr>
<td>MG-1283</td>
<td>300</td>
<td>Monitoring</td>
<td>Down</td>
<td>6.1</td>
</tr>
</tbody>
</table>

VOCs detected in borehole flow are summarized in table 2. Fluid from all boreholes sampled contained detectable concentrations of VOCs. Of 37 VOCs analyzed for, 19 (51 percent) were detected. Trichloroethylene (TCE) and tetrachloroethylene (PCE) were detected in samples from all boreholes. Chloroform, 1,1,1-trichloroethane (TCA), and trans-1,2-dichloroethylene (DCE) were detected in eight of nine boreholes sampled. The source of chloroform in groundwater may be leaking water-distribution and sewer lines in the study area. Some compounds, such as trans-DCE, 1,1-dichloroethane (DCA), and vinyl chloride (VC) were never used in the study area and are degradation products of other VOCs. Under anaerobic conditions, PCE successively degrades by reductive dechlorination to TCE, cis-DCE or trans-DCE, 1,1-dichloroethene, and VC (Parsons and others, 1984; Vogel and McCarty, 1985; Freeman and Gossett, 1989). TCA anaerobically degrades to DCA. Concentrations of TCE, TCA, and 1,1-dichloroethylene in borehole-fluid samples as great as 5,800 µg/L, 1,400 µg/L, and 260 µg/L, respectively, indicate that some of the water moving downward in the aquifer through open boreholes is highly contaminated and that open boreholes may contribute substantially to groundwater contamination.
### Table 2. Volatile organic compounds detected in borehole-flow samples

[Concentrations given in micrograms per liter]

<table>
<thead>
<tr>
<th>Compound</th>
<th>Number of boreholes in which compound was detected</th>
<th>Maximum concentration detected</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>1</td>
<td>0.5</td>
</tr>
<tr>
<td>Bromoform</td>
<td>1</td>
<td>.4</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>4</td>
<td>25</td>
</tr>
<tr>
<td>Chlorodibromomethane</td>
<td>1</td>
<td>.2</td>
</tr>
<tr>
<td>Chloroform</td>
<td>8</td>
<td>15</td>
</tr>
<tr>
<td>Dichlorobromomethane</td>
<td>2</td>
<td>.4</td>
</tr>
<tr>
<td>1,1-Dichloroethane</td>
<td>6</td>
<td>14</td>
</tr>
<tr>
<td>1,2-Dichloroethane</td>
<td>2</td>
<td>5.6</td>
</tr>
<tr>
<td>1,1-Dichloroethylene</td>
<td>6</td>
<td>260</td>
</tr>
<tr>
<td>trans- and cis-1,2-Dichloroethylene</td>
<td>8</td>
<td>72</td>
</tr>
<tr>
<td>1,2-Dichloropropane</td>
<td>2</td>
<td>60</td>
</tr>
<tr>
<td>Methylene chloride</td>
<td>3</td>
<td>.4</td>
</tr>
<tr>
<td>Tetrachloroethylene</td>
<td>9</td>
<td>57</td>
</tr>
<tr>
<td>Toluene</td>
<td>1</td>
<td>.2</td>
</tr>
<tr>
<td>1,1,1-Trichloroethane</td>
<td>8</td>
<td>1,400</td>
</tr>
<tr>
<td>1,1,2-Trichloroethane</td>
<td>2</td>
<td>.4</td>
</tr>
<tr>
<td>Trichloroethylene</td>
<td>9</td>
<td>5,800</td>
</tr>
<tr>
<td>Trichlorofluoromethane</td>
<td>1</td>
<td>.9</td>
</tr>
<tr>
<td>Vinyl chloride</td>
<td>2</td>
<td>1.4</td>
</tr>
</tbody>
</table>

**CROSS-CONTAMINATION BY VOLATILE ORGANIC COMPOUNDS**

The rate of borehole-fluid movement is known; therefore, concentrations of VOCs in borehole-fluid samples can be used to estimate the downward mass flux and the extent of aquifer cross-contamination. The mass of a VOC moving downward in the aquifer through an open borehole annually was estimate based on the measured borehole-flow rate and results of chemical analysis of the fluid by:

\[
M = 1.99 \times Q \times C, \tag{2}
\]

where \(M\) is the quantity of a compound moving down a borehole annually, in grams per year; \(Q\) is the measured borehole flow, in gallons per minute; and \(C\) is the concentration of the compound in the borehole fluid, in micrograms per liter.

Because most of the wells were sampled once and concentrations of VOCs vary temporally, the mass flux estimates should be considered an approximation. The data can be used to provide an estimate of the magnitude of cross-contamination. An estimated 80.9 kg/yr of VOCs (table 3) were moving downward through the nine open boreholes sampled from the contaminated, upper part of the aquifer to the lower part. Trichloroethylene accounts for 94 percent and 1,1,1-trichloroethane accounts for 3 percent of the compounds.
### Table 3. Estimated quantity of volatile organic compounds moving downward in the Stockton Formation through nine sampled boreholes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Grams per year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon tetrachloride</td>
<td>566</td>
</tr>
<tr>
<td>1,1-Dichloroethane</td>
<td>203</td>
</tr>
<tr>
<td>1,2-Dichloroethane</td>
<td>8.2</td>
</tr>
<tr>
<td>Chloroform</td>
<td>35.7</td>
</tr>
<tr>
<td>1,1-Dichloroethylene</td>
<td>727</td>
</tr>
<tr>
<td>trans- and cis-1,2-Dichloroethylene</td>
<td>246</td>
</tr>
<tr>
<td>1,2-Dichloropropane</td>
<td>449</td>
</tr>
<tr>
<td>Tetrachloroethylene</td>
<td>449</td>
</tr>
<tr>
<td>1,1,1-Trichloroethane</td>
<td>2,049</td>
</tr>
<tr>
<td>1,1,2-Trichloroethane</td>
<td>1</td>
</tr>
<tr>
<td>Trichloroethylene</td>
<td>75,861</td>
</tr>
<tr>
<td>Total</td>
<td>80,851</td>
</tr>
</tbody>
</table>

### CONCLUSIONS

A combination of borehole geophysical methods, measurements of vertical borehole flow, and analyses of borehole-fluid samples provided effective methods to identify and assess an aquifer cross-contamination problem. Borehole geophysical methods were used to identify zones of fluid movement. Borehole-flow measurements provided data on the direction and rate of borehole-fluid movement. Sampling and analysis of moving borehole fluid provided concentrations of VOCs. An estimated 80.9 kg/yr of VOCs (table 3) were moving downward through the nine open boreholes sampled from the contaminated, upper part of the aquifer to the lower part, which is tapped by public-supply wells. This magnitude of this flow indicates that cross-contamination caused through open boreholes is a serious problem affecting ground-water supplies.

In response to a verbal presentation of study results, the USEPA Superfund Removal Branch plugged or reconstructed five of the sampled boreholes plus four other boreholes. The remaining four sampled boreholes were reconstructed by the USGS so that they are now open only to a single water-bearing zone. Wells in the six monitoring clusters on the Raymark NPL site were constructed or reconstructed by the USEPA so that they are open only to a single water-bearing zone. The aquifer cross-contamination problem caused by known boreholes in the study area has been eliminated.

### REFERENCES


A Sample-Freezing Drive Shoe for a Wireline-Piston Core Sampler

By Fred Murphy and W.N. Herkelrath

Abstract

The loss of fluids and sample during retrieval of cores of noncohesive sediments results in incorrect measures of fluid distributions and a less-than-ideal measure of the stratigraphic position of the sample. In order to reduce these errors, a hollow drive shoe was developed that allows freezing in place the lowest 75 millimeters of a 48-millimeter-diameter, 1.5-meter-long sediment sample taken using a commercial wireline piston-core sampler. The end of the core is frozen by piping liquid carbon dioxide at ambient temperature through a steel tube from a bottle at the land surface to the drive shoe where it evaporates and expands, cooling the interior surface of the shoe to about -70 °C. The freezing process takes about 10 minutes. This device was used to collect samples for a study of oil-water-air distributions in unconsolidated sediments at the site of an oil spill near Bemidji, Minnesota. Before freezing was employed, samples of sandy sediments from near the water table sometimes flowed out of the core barrel as the sampler was withdrawn. Freezing the bottom of the core ensured the retention of all material that entered the core barrel and lessened the redistribution of fluids within the core.

INTRODUCTION

Because saturated, noncemented, well sorted sands have high permeability and low cohesion, collection of core samples without losing sediment or pore fluids as the sampler is removed from its position after driving is difficult. Various devices have been used to reduce sample loss, including pistons or remotely operated valves that maintain a vacuum above the sample (Munch and Killey, 1985; Zapico and others, 1987). Inflatable bladders that expand into and seal the lower end of a core barrel (McElwee and others, 1991), movable steel fingers that are driven into the sediment just below the core liner (McElwee and others, 1991), and sample-freezing jackets (Durnford and others, 1991). Munch and Killey (1985) and Zapico and others (1987) incorporated a left-hand-threaded coupling between the drill string and the core barrel to allow the core barrel to be detached from the drill string and retrieved rapidly by means of a wireline.

The hollow drive shoe described in this paper (fig. 1) enables freezing in place of the lowest 75 mm of a 48-mm-diameter, 1.5-m-long core after the core sampler has been driven. The hollow drive shoe replaces the standard drive shoe of the Solinst wireline-piston core sampler (Zapico and others, 1987). Interstitial ice in the frozen sediment prevents fluid from flowing through it, and friction between the ice-sediment plug and the plastic core liner prevents the otherwise free-flowing sand from leaving the core barrel liner. The purpose of this paper is to describe the design, fabrication, and field use of the freezing sampler.

BACKGROUND

In 1979, a broken high-pressure pipeline spewed about 2x10^6 L of crude oil over several thousand square meters of sandy glacial outwash deposits near Bemidji, Minn. (fig. 2). The impetus for developing the sample-freezing drive shoe was the difficulty we experienced in recovering cores of saturated and nearly saturated sands at the Bemidji site by means of a simple wireline-piston core sampler. The core samples are needed to measure the distributions of oil, air, and water within the sediments in connection with modeling the movement of the oil at the site (Hess and others, 1992; Essaid and others, 1993).
Figure 1. A cross-sectional view of the sample-freezing drive shoe attached to the Solinst core barrel. The scale is broken—the sampler is about 2-m long and 75-mm in diameter.
DESCRIPTION OF THE DEVICE

The sample-freezing drive shoe (fig. 3) is a triple-walled steel cylinder that threads onto the Solinst core barrel in place of the standard, solid, hardened-steel drive shoe. The device is assembled from brazed and welded mild-steel parts except for the cutting edge of the drive shoe, which is faced with a hard alloy for wear resistance.

In order to freeze the bottom end of a core sample, liquid carbon dioxide is sprayed into the lower end of the inner chamber. The liquid evaporates, depositing solid carbon dioxide (dry ice) at about -70 °C in the distribution channels cut in the inner wall of the freezing chamber (fig. 3). As the dry ice sublimes, and the liquid evaporates, the resulting carbon dioxide gas circulates upward through the channels, exhausts through holes in the upper end of the interior wall, moves through the annulus between the plastic core liner and the core barrel, passes from the exterior of the liner to its interior through slots in the upper end of the liner, and leaves the sampler through the cable hole in the core barrel cap.

Flow of carbon dioxide is restricted near the entry of the feed tube to the freezing chamber by a 1.5-mm-diameter wire that occupies most of the 1.9-mm bore of a 10-cm length of stainless-steel tubing. This restriction ensures that the carbon dioxide remains a liquid under a pressure of about 6000 kPa within the feed tube. Carbon dioxide vaporization and resulting cooling only occurs downstream from the restriction within the freezing chamber; this cools the sample efficiently and prevents ice from binding the feed tube to the sediment.

USE OF THE SAMPLE-FREEZING DRIVE SHOE

Use of the freezing sampler in the field is shown in figure 4. Carbon dioxide is piped from a bottle equipped with a dip tube, through a short length of flexible tubing, and then through segments of 1/4-inch outside-diameter stainless-steel tubing to the drive shoe. The upper pieces of tubing are interchangeable 1.52-m-long segments, but the two lowest sections of tubing are special. The tube that attaches to the drive shoe extends without a break from the drive shoe to above the core barrel cap; this tube includes a thick-walled, threaded lower section about 10-cm long that fits a mating part of the drive shoe. A filter attached to the upper end of the tube prevents particles from entering the drive shoe and plugging the flow-restricting narrow tube in the shoe. The next segment of tubing above the drive shoe has a U-shaped fold that is refolded to fit snugly against the drive rod used to emplace the sampler. This double bend makes the feed tube assembly slightly elastic and so prevents breakage of the tube joints when the feed tube scrapes or catches on the auger during driving.

In use, the core barrel is assembled with a 1.75-m-long piece of polycarbonate liner fitted between shoulders cut in the drive shoe and in the core barrel cap. The piston is passed through the liner and set in the nose of the drive shoe, and the core barrel cap is threaded onto the sampler. The core sampler is placed in the bore of the auger and lowered to the bottom of the hole. The 1.52-m-long segments of carbon-dioxide feed tubing are attached to the sampler as it is lowered. Once the sampler is in place at the bottom of the bore, the wire-line is pulled taut, and the sampler is hammered 1.52 m into the ground.

After the sampler has been driven, the carbon dioxide bottle is attached to the feed tube through a short length of flexible tubing. The tank valve is opened, and a 1/8-inch ball valve is opened to allow liquid carbon dioxide to flow to the drive shoe. A hissing or bubbling sound made by the escaping gas can usually be heard coming from inside the auger. When the drive shoe becomes plugged with solid carbon dioxide, the noise stops or becomes intermittent, and the valve is closed. Closure of the valve prevents possible damage to the drive shoe from the pressure of liquid carbon dioxide and reduces unnecessary chilling of
Figure 3. (A) An exploded view of the sample-freezing drive shoe. (B and C) Two transparent views of the assembled device, shown rotated 90 degrees with respect to each other.
Figure 4. A partly transparent view of the emplaced sample-freezing drive shoe as it might appear during the freezing operation.
the exterior of the drive shoe. After a minute or so, the sputtering sound will settle to a steady hiss, or, if the shoe has been completely plugged, the hissing will resume. The valve can again be opened until the shoe again plugs with dry ice. This process is repeated until about 10 minutes have elapsed. The lowest 75 mm of the sample will then be frozen.

Although the drive shoe is triple walled and the exterior near the freezing jacket is insulated by an air gap, ice does adhere to the exterior of the shoe. Sometimes the use of the drill rig's hydraulic cylinders was necessary to break the sampler loose from the bore. Once the sampler is loose it can be recovered on the drill string by means of a winch. The sample end remains frozen for several minutes. To date this device has been used to collect about 20 cores. The device was successfully used to sample at depths more than 2 m below the water table.

DISCUSSION

Use of the sample-freezing drive shoe takes more time and effort than using a simple wireline-piston core sampler. When the core end is frozen, the use of a piston is not necessary to retain sediment in the core barrel. However, the piston does prevent loose material and fluid, particularly oil floating on water in the bore, from contaminating the sample. Judging from the preservation of laminae and sharp interfaces in the cores that have been retrieved, samples recovered using the sample-freezing drive shoe appear to be no more disturbed than those collected by means of the standard drive shoe with the Solinst sampler.

Poor sample recovery can have several causes; for example, a cobble could jam in and plug the drive shoe opening, the material through which the barrel is being driven could be compressed or forced aside by the drive shoe and not enter the core barrel, or the end of the core barrel liner could fold into the interior of the drive shoe and prevent sediment from entering. The sample-freezing drive shoe ensures only that all material that enters a core barrel is retained there and lessens the redistribution of fluids in the sample.

The cryogenic sampler described by Durnford and others (1991) is similar to the device described here in that both samplers use bottled carbon dioxide to freeze core samples. That device is described as being capable of retrieving 32-mm-diameter, 75-mm-long cores over a depth range of 1.2 to 1.8 m, does not employ a piston, and is not adaptable to a commercially available core sampling tool. The sampler described in this note can be used to obtain larger cores (47 mm diameter and 1.5 m long) from depths of at least 8 m, but it is of a more complex design than the sampler described by Durnford and others (1991) and has a larger outside diameter. The sample-freezing drive shoe described here requires an auger with an inside diameter of at least 90 mm, whereas the sampler described by Durnford could be passed through an auger with a smaller bore.

SUMMARY AND CONCLUSIONS

A hollow drive shoe was developed that is compatible with a commercially available core-sampling tool that freezes the lowest 75-mm of a core after the sampler is emplaced. In-place freezing of the end of a core of noncohesive sediment prevents the loss of any material that enters the barrel and lessens the redistribution of fluids as the sample is retrieved and during subsequent handling. The time needed to collect a sample is somewhat greater when the sample-freezing drive shoe is used, because time is needed to assemble and disassemble the carbon dioxide feed tubes, and about 10 minutes is needed to freeze the core end. The sample-freezing drive shoe offers a means to enhance recovery of samples of noncohesive materials and the fluids they contain from the shallow saturated zone.

REFERENCES


Determination of Surface Area of Soil Components by Sorption of Nitrogen and Ethylene Glycol Monoethyl Ether Vapors and Evaluation of Adsorption, Partition and Cation Solvation Processes

By Cary T. Chiou and David W. Rutherford

Abstract

The vapor uptake isotherms of nitrogen and ethylene glycol monoethyl ether (EGME) were determined for soil and soil components. The cross sectional area of EGME was determined to be $40.0 \times 10^{-20}$ m$^2$ by comparing adsorption isotherms on reference surface area standards. For samples where EGME does not penetrate into the solid (Ottawa Sand, hematite, aluminum oxide, synthetic hydrous iron oxide, and kaolinite), the EGME and nitrogen isotherms show consistent surface uptake and the EGME isotherm can be reasonably estimated from the nitrogen isotherm by multiplying the nitrogen uptake by a factor of 1.3 to account for different molecular area and molecular weight. For other samples where the EGME can penetrate into the solid (peat, Ca-montmorillonite, and illite), the total uptake can be resolved to surface adsorption, partition into soil organic matter, and/or cation solvation. For peat, the nitrogen uptake is very small, resulting in a surface area of 1.3 square meters per gram; uptake of EGME on peat is large and linear, which is indicative of large bulk solubility of EGME in soil organic matter (190 milligrams per gram). For Ca-montmorillonite, the resulting cation solvation isotherm shows a stoichiometric interaction of about 4 EGME molecules per exchangeable Ca ion. Exchange of organic cations for metal ions in montmorillonite sharply decreases the cation solvation effect of EGME. This cation exchange may result in a higher surface area of the clay due to opening of interlayer surfaces.

INTRODUCTION

Because of various molecular components and lattice structures in such solids as soils, minerals, and clays, these materials may exhibit multiple interactions in the sorption of specific chemical species. While experimental sorption data reflect the total uptake from all contributing mechanisms, it is of practical interest to determine the relative contributions to the observed uptake from all of these interactions. In principle, the uptake of a chemical by a solid can result either from its adsorption on the solid’s intrinsic (external) surfaces or from its penetration into the solid’s internal matrix by processes other than surface adsorption, such as cation solvation in expanding clays or the dissolution into a portion of the solid matrix. To separate these contributions, one begins by determining the uptake capacity by one (or more than one) of the mechanisms using unequivocal analytical methods and subtracting it from the total capacity and repeating this process in a step-wise manner.

For a chemically inert vapor showing no specific reaction or penetration effect, its uptake by a solid results mainly from physical adsorption on the solid’s surfaces. In such cases, the adsorption ranging from submonolayer to multilayer capacity can be well characterized by the Brunauer-Emmett-Teller (BET) model (Brunauer and others, 1938). In systems where vapors penetrate into the solid, the observed sorption...
capacity would exceed the amount predicted by the BET equation. It is, therefore, prudent to analyze the vapor sorption by the BET equation for the vapor/solid pair of interest in comparison with the capacity of a reference inert gas (such as nitrogen) on the same solid to account for the extent of uptake attributable to chemical penetration.

This paper describes the uptake of a nonpolar vapor (nitrogen) and a polar vapor (ethylene glycol monoethyl ether) (EGME) on soil organic matter (peat), kaolinite, Ca-montmorillonite, and two organo-clays, and the analysis of individual effects of surface adsorption, bulk solubility, and cation solvation pertinent to the system. In soil science, it has been assumed that the uptake of polar EGME measures the “total surface” of a solid, while the uptake of nonpolar nitrogen measures the external surface of the solid (Dyal and Hendricks, 1950; Bower and Gschwend, 1952; Martin, 1955; Sor and Kemper, 1959); the difference has been described as “internal surface.” It is arguable that the term “internal surface” is appropriate, since the difference in uptake caused by penetration of a polar solvent (or vapor) can be more properly attributed either to the cation solvation effect (as in expanding clays) (Tiller and Smith, 1990; McNeal, 1964; Dowdy and Mortland, 1967) or to solubility (as in soil organic matter) (Chiou and others, 1990; Chiou and others, 1988; Rutherford and others, 1992).

**Experimental**

Two surface-area reference standard samples of aluminum oxide were used; surface areas were 109 m$^2$/g (reference standard A) and of 29.9 m$^2$/g (reference standard B). An additional aluminum oxide sample (nonactivated reagent grade) had a purity of 99.99 percent. The Ottawa sand is a standard sand with a 20 to 30 mesh particle size. The sample was washed with 10 percent HCl and treated with H$_2$O$_2$ to remove any residual iron oxides and organic matter. The hematite sample was highly pure with a total Fe content of 70.28 percent on a dry-weight basis; X-ray diffraction data showed the sample to be a well-crystallized material. The synthetic hydrous iron oxide was prepared in the laboratory by hydrolyzing 0.5 M aqueous ferric nitrate with 10 percent NaOH at pH 8.0 to 8.5. The sample has a total Fe content of 62.4 percent. X-ray diffraction data showed it to be an essentially amorphous iron oxide with low goethite content. The Ca-montmorillonite sample had a cation exchange capacity of 120 meq/100 g. The fifthian illite sample contained greater than 90 percent illite (with minor amounts of quartz and muscovite), had a cation exchange capacity of about 25 meq/100 q (with K as the major cation), and an organic carbon content of about 0.8 percent. The illite sample was treated with H$_2$O$_2$ to reduce the organic content before its use in sorption experiments. The treated sample contains about 0.4 percent organic carbon. The peat sample is a reference peat of the International Humic Substances Society, collected from the Everglades, FL. Reagent grade tetramethylammonium (TMA) bromide and tetraethylammonium (TEA) bromide were used. Woodburn soil is a silt loam from Oregon and its dry-weight composition is 1.9 percent organic matter, 68 percent silt, 21 percent clay, and 9 percent sand. X-ray diffraction showed that fine-grained mica (illite) and kaolinite are the dominant clays.

The TMA and TEA exchanged montmorillonites were prepared by suspending 10 g of Ca-montmorillonite in 800 mL of water. Approximately 3 mol of the organic cation per mol of cation exchange capacity (CEC) was added and mixed for 24 hours. The suspension was washed on a filter membrane until a bromide test with AgNO$_3$ was negative. Organic carbon analysis showed that the TMA-montmorillonite was 87 percent exchanged with TMA and the TEA-montmorillonite 73 percent exchanged with TEA.

The apparatus and procedure used for the determination of vapor uptake by soils and minerals has been described previously (Chiou and others, 1988). Briefly, the experiment consisted of equilibrating the vapor in a sorption chamber containing an electronic microbalance from which a test solid sample (sorbent) was suspended in a small glass cup. The sorbent sample was heated at 100 °C for 8 to 10 hours inside the chamber and then cooled to room temperature for 6 to 8 hours under a vacuum of 10$^{-6}$ torr to remove moisture and to determine the “dry sample weight.” Typically, 100 to 500 mg of sample was used in sorption experiments. The test liquid (EGME) was purified by vacuum distillation to remove residual air and then introduced into the sorption chamber to equilibrate. A change in sample weight resulting from vapor uptake was recorded as an electrical signal from the balance. The partial pressure of EGME at the point of vapor-sample equilibrium was recorded by a pressure gauge. The saturation vapor pressure of EGME at room temperature (about 5 mm Hg at 24 °C) was determined by
monitoring the pressure of saturated EGME vapor prior to the sorption experiment.

The vapor uptake of nitrogen gas by the sample was determined at liquid nitrogen temperature using a surface area analyzer. The test samples were prepared by heating at 100 °C under a flow of pure nitrogen gas for 24 hours. The surface areas of samples were calculated by use of the linear BET plot of the nitrogen isotherms at relative pressures of 0.05 to 0.30 to obtain the monolayer adsorption capacities, together with the cross sectional area of the nitrogen molecule.

RESULTS AND DISCUSSION

For surface adsorption, according to the BET theory (Brunauer and others, 1938), the adsorption capacity at the beginning of the linear range following the initial sharp rise corresponds roughly to the completion of monolayer adsorption (Q_m); multilayer adsorption is signified by increasing slope of the isotherm as the relative pressure approaches 1. The Q_m value of the adsorbate and the proper molecular area (a_m) of the adsorbate are then used to calculate the surface area of the solid (adsorbent). The linear BET plot allows the value of Q_m of an adsorbate on a given solid to be calculated, as follows:

\[
\frac{1}{Q(P/P^0)} = \frac{C}{CQ_m P^0} + \frac{1}{CQ_m} \quad (1)
\]

where Q is the amount of vapor adsorbed at given P/P^0, P is the equilibrium partial pressure of the adsorbate, P^0 is the saturation vapor pressure of the adsorbate, and C is a constant related to the net heat of monolayer adsorption, which affects the sharpness of the curvature. A plot of 1/Q(P/P^0) against P/P^0 yields a straight line with a slope of (C-1)/CQ_m and an intercept of 1/CQ_m, from which the Q_m and C values are calculated. The linearity of the BET plot is usually observed at P/P^0 = 0.05 - 0.30 in systems involving physical adsorption (Brunauer and others, 1938; Dyal and Hendricks, 1950; Bower and Gschwend, 1952). The cross sectional area of 16.2 x 10^-20 m^2 for the nitrogen molecule is well established from the literature (Brunauer and others, 1938; Dyal and Hendricks, 1950; Bower and Gschwend, 1952). To determine the molecular area of EGME, we determined the EGME monolayer capacities of two alumina reference samples (29.9 and 109 m^2/g, respectively) as 11.3 and 40.4 mg/g from the BET plot (eq. 1) of the respective EGME isotherms; the EGME corresponding cross sectional areas are 39.6 x 10^-20 and 40.4 x 10^-20 m^2, giving an average of 40.0 x 10^-20 m^2.

The BET model describes vapor adsorption on surfaces that are external to the solid. This adsorption may include penetration into pores but not into the solid matrix. In cases where penetration of the solid matrix occurs along with surface adsorption, the system may exhibit an “apparent monolayer capacity” giving a higher “apparent surface area.” Therefore, a comparison of the “apparent monolayer capacity” from a vapor (such as EGME) that could potentially penetrate into a solid sample with the surface area of the solid characterized by an inert vapor (such as N_2) provides a measure of the uptake by penetration of the vapor.

The isotherms for nitrogen and EGME uptake by kaolinite are shown in figure 1. These isotherms are typical of a type II isotherm, which is characteristic of the transition from submonolayer to multilayer surface adsorption. The surface area calculated from the BET equation is 21.0 m^2/g using the nitrogen isotherm and 21.1 m^2/g using the EGME isotherm. This shows the consistency of the BET method in determining the surface uptake of vapors, as long as the vapors do not penetrate the solid matrix. The equivalence of nitrogen and EGME isotherms for other nonswelling mineral samples (sand, hematite, aluminum oxide, and synthetic iron oxide) is also demonstrated and is shown in table 1.

![Figure 1. Isotherms of ethylene glycol monoethyl ether vapor at room temperature and nitrogen vapor at 77 °K for kaolinite and Florida peat.](image-url)
Table 1. \( Q_m(N_2) \) monolayer capacities, BET-(\( N_2 \)) surface areas, \( Q_m(EGME)_{eq} \) equivalent monolayer capacities, and \( Q_m(EGME)_{ap} \) apparent monolayer capacities of selected soils and minerals

[The \( Q_m(N_2) \) values are from \( N_2 \) adsorption isotherms and the BET equation; \( Q_m(N_2) \) values are used to determine the surface areas of samples; the \( Q_m(EGME)_{eq} \) values are equivalent to \( Q_m(N_2) \) for the same surface areas of samples; \( Q(EGME)_{ap} \) values are from the EGME sorption isotherms and the BET equation, assuming that no penetration or specific interaction occurs. The ratio of \( Q_{ap}(EGME) \) to \( Q_{eq}(EGME) \) when significantly greater than 1, expresses the extent of EGME penetration or specific interaction.]

<table>
<thead>
<tr>
<th>Sample</th>
<th>( Q_m(N_2) ) (mg/g)</th>
<th>BET-(( N_2 )) Area (m²/g)</th>
<th>( Q_m(EGME)_{eq} ) (mg/g)</th>
<th>( Q_m(EGME)_{ap} ) (mg/g)</th>
<th>( Q_m(EGME)<em>{ap}/Q_m(EGME)</em>{eq} )</th>
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<tbody>
<tr>
<td>Ottawa Sand</td>
<td>0.032</td>
<td>0.11</td>
<td>0.042</td>
<td>0.035</td>
<td>0.83</td>
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<td>.90</td>
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<tr>
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<td>.88</td>
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<td>Kaolinite</td>
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<td>.47</td>
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<tr>
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<td>4.19</td>
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<td>3.20</td>
</tr>
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</table>

The isotherms for nitrogen and EGME on peat are shown in figure 1. The nitrogen isotherm is type II, whereas the EGME isotherm shows a large and linear uptake that is characteristic of bulk EGME solubility in peat (Chiou and others, 1990; Chiou and others, 1988; Rutherford and others, 1992). The nitrogen isotherm gives a surface area of 1.5 m²/g. Because the EGME isotherm on peat is linear (rather than type II), the BET calculation does not apply; obviously, the small EGME adsorption is obscured by the much larger partition effect with peat. The limiting solubility of EGME in peat at \( P/P_0 = 1 \), normalized for the organic content of peat, is 190 mg/g.

As shown above, in the absence of vapor penetration, nitrogen and EGME isotherms give equivalent surface coverage; therefore, the nitrogen isotherm can be converted to an equivalent EGME isotherm for surface adsorption by multiplying the nitrogen adsorption capacity by a factor of 1.3, to account for differences in molecular weights and molecular cross sectional areas. This procedure was applied to vapor sorption by Ca-montmorillonite, fifthian illite, and two organoclays to account for surface adsorption on (preexisting) external surfaces (from nitrogen adsorption data).

The amount of EGME penetration was then determined from the difference of the total EGME isotherm and the calculated EGME isotherm for surface adsorption and is plotted as the EGME cation solvation isotherm. The original EGME and nitrogen isotherms and the EGME cation solvation isotherm for Ca-montmorillonite are shown in figure 2.

![Figure 2. Isotherms of ethylene glycol monomethyl ether vapor at room temperature and nitrogen vapor at 77 °K on Ca-montmorillonite.](image-url)
The equivalent EGME monolayer capacity [$Q_m^{(EGME)}_{eq}$] calculated from the nitrogen monolayer capacity and apparent EGME monolayer capacity [$Q_m^{(EGME)}_{ap}$] calculated from the EGME uptake isotherm using the BET equation for all samples are summarized in Table 1. The $Q_m^{(EGME)}_{ap}$ for Ca-Montmorillonite is 7.6 times higher than the $Q_m^{(EGME)}_{eq}$. The ratio of $Q_m^{(EGME)}_{ap}$ to $Q_m^{(EGME)}_{eq}$ is 1.5 illite, 1.4 for TMA-montmorillonit, and 1.8 for TEA-montmorillonite. The large ratio for Ca-montmorillonite is attributed to the large cation solvation effect of EGME relative to its surface adsorption. The EGME cation solvation isotherm in figure 2 shows rapid uptake of EGME at relative pressures below 0.1 and complete solvation above this point as indicated by the relatively flat isotherm. Based on CEC of 120 meq/100g, this would indicate a stoichiometric relation of about 4 EGME molecules per exchangeable Ca ion. The smaller ratio for illite is in keeping with its lower CEC (15.5 meq/100g) and the lower cation solvation of EGME with K relative to Ca (0.9 - 1.4 EGME molecules per exchangeable K ion). Similarly, substitution of TMA or TEA for Ca in the montmorillonite decreases the cation solvation effect, as these organic cations are presumably less effectively solvated by EGME than the Ca ion. In case of TMA-montmorillonite, a great increase in surface area is noted over that of Ca-montmorillonite, indicating that the interlayer opened up by TMA ions is relatively accessible to nitrogen and EGME. This is not observed for TEA-montmorillonite since the surface area remains comparable with that of Ca-montmorillonite, indicating that the bigger TEA ions occupy most of the interlayer space.

As shown, the uptake of polar vapors (as EGME) by dry natural samples may be expected to occur by multiple mechanisms, including surface adsorption on external surfaces, partition (dissolution) into the sample’s organic matter (or organic impurities), and solvation of the interlayer cations in expanding clays. The significance of each interaction depends on the composition and morphology of the solid samples as well as on the polarity of vapors. In general, as the polarity of the vapors decreases, both the partition effect with organic matter and the cation solvation effect decrease. The expected decrease in partition follows from the observation that the solubility of vapors or liquids in relatively polar soil organic matter increases sharply with the polarity of the vapors or liquids (Chiou and others, 1990). The expected decrease in cation solvation has been demonstrated from published data showing the consistency of the nitrogen and nonpolar organic vapor uptake by expanding clays and the excess uptake of polar compounds, as demonstrated in this study.

A general analytical procedure to determine the relative contributions of surface adsorption, partition, and cation solvation for sorption of a vapor on a natural solid sample containing clays, other inorganic matter, and organic matter would involve (1) determination of the sorption isotherms of the vapor of interest and of nitrogen on the sample (2) determination of the sample’s organic and ash contents (3) subtraction of the portion of the non-penetrating vapor isotherm (calculated from the nitrogen isotherm using a suitable conversion factor) from the total isotherm, and (4) subtraction from the resulting curve of the linear isotherm calculated for the organic content of the sample. The last step requires either the experimental or the estimated vapor sorption (partition) isotherm on soil organic matter. The result from the above procedure would give an isotherm that can be used to estimate the cation solvation contribution. This procedure has been applied to Woodburn soil as shown in figure 3.

**SUMMARY**

The differences in sorption capacities of polar EGME and nonpolar, inert N₂ on various dry solids illustrate the various interactions that control the vapor uptake. The extent of physical adsorption on a solid’s
surfaces can be accounted for by BET equation using the nitrogen adsorption data and a constant adjusting factor. The excess over physical adsorption on the solid’s surfaces is attributed to either vapor solubility in SOM or cation solvation with clay components. The procedure used to separate these effects for EGME sorption can be used to separate the different sorptive contributions of other organic vapors on a natural solid. Thus, the sorption of nonpolar vapors (such as aliphatic and aromatic hydrocarbons) on dry soils and minerals should consist primarily of surface adsorption, because nonpolar vapors have low solubility in polar SOM and cannot effectively solvate clay cations. This result has been verified by the consistency of the total uptake of various low-polarity vapors on soils in comparison with the nitrogen adsorption data in an earlier study. The sorption capacities of polar liquids or vapors on dry natural solids may be expected to be greatly enhanced over their surface adsorption capacities if these samples contain significant amounts of organic matter and/or solvating clays because of the concurring solubility in SOM and/or the cation solvation effect.

REFERENCES


Isolation of Lipophilic Organic Contaminants along the Upper Mississippi River Using a Semipermeable Membrane Device

By Geoffrey S. Ellis1 and Colleen E. Rostad1

Abstract

The detection of many environmental contaminants in water is often hindered by their transient nature and low concentration. However, these compounds can represent a significant environmental hazard to biota and humans through bioconcentration. Traditional methods of analyzing aquatic biota are complicated by variations in species, sex, age, reproductive stage, location, behavioral patterns, metabolism, and water conditions. A new sampling device consisting of a tubular semipermeable membrane of low-density polyethylene filled with synthetic fish fat, trioliene, which mimics the mechanism of bioconcentration, may resolve some of these problems. To evaluate the effectiveness of these sampling devices, they were deployed at nine sites along the upper Mississippi River; caged fish at three of these sites were used for comparison purposes. The devices and caged fish were collected over an eight-week period, and indigenous fish were collected at the end of the study. Compounds were extracted from the trioliene by back dialysis into an appropriate solvent. Fish tissues were ground and extracted wet into a solvent and the lipid removed. All samples were analyzed by gas chromatography/mass spectrometry (GC/MS). Target compounds were pesticides, herbicides, and polychlorinated biphenyls (PCBs). Comparisons of compound concentrations in the fish samples and sampling devices will be used to determine the effectiveness of this technique as a monitoring tool for bioconcentration.

INTRODUCTION

The uptake and concentration of lipophilic organic contaminants by aquatic organisms is a significant pathway for toxic compounds in the environment. In conjunction with food chain effects, this constitutes bioaccumulation which magnifies concentrations of chemicals in fatty tissues of organisms in successively higher trophic levels (Neely, 1980). This process has the potential to increase the toxicological significance of all lipophilic contaminants in the environment. Although the bioavailability of toxins in the environment is of great importance for human health and environmental quality concerns, it is often difficult to assess. The transient nature of direct chemical discharges and low concentrations of many nonpoint-source contaminants in the water column frequently preclude compound detection and quantification due to limitations of sampling and analytical technology.

Historically, bioavailability has been described in terms of equilibrium partitioning models, which attempt to express this process mathematically in terms of two compartments and the flux rates into and out of the compartments. Aquatic organisms are viewed as lipid pools separated from an aqueous medium by a biomembrane. Flux rates are assumed to be determined by passive diffusion of contaminants across the membrane. Although these models generally correct for differences in percent lipid between individual organisms, they assume that lipid-water partitioning is independent of known variations in lipid composition and content between species, and age and gender differences within a species. These models often rely on empirically derived partition coefficients between an organic solvent and water (usually octanol-water systems expressed as KoW) however, these constants may not be sufficiently representative of actual bioconcentration factors (Huckins and others, 1990, Opperhuizen and others, 1988).

Several other factors complicate the application of equilibrium partitioning models to complex environmental systems. The area in which organisms are found may range from a static location for immotile organisms to thousands of kilometers for migratory species; this areal variability can confound efforts to identify sources and pathways for the compounds of interest. Many absorbed contaminants are metabolized by organisms to other compounds which also may be toxic, and some or all of these metabolic products may be excreted on a relatively short time scale. Bioavailability studies typically require large numbers of biological samples that are very time consuming and labor intensive to collect and analyze. Consequently, the specific processes involved in bioaccumulation have been completely determined for only relatively simple environmental systems.

By the late 1970’s, these problems were well documented and efforts were being made to address them. In 1980, Bryne and Aylott (1980) received a British patent for a passive sampling device based on liquid-liquid partitioning between a nonpolar solvent and water separated by a semipermeable membrane. Sodergren (1987) was the first to use a hydrophilic dialysis membrane filled with hexane. These devices have many advantages over conventional biomonitoring. Absorbed compounds are not metabolized and variations among different species with respect to gender, age, lipid content, and so forth are eliminated, and the location of the sampling site is fixed.

Although these methods represent distinct advantages over previous methods, several problems are associated with them. Because the process of diffusion across a semipermeable membrane is essentially passive through small pores in the membrane, low-molecular-weight compounds may pass through the membrane unimpeded; whereas comparatively large molecules are excluded. The Solvents used inside these semipermeable membrane devices (SPMDs) are low molecular weight and, therefore, tend to diffuse out of the sampling device by osmotic pressure. Over long periods of time, these solvent losses can be significant. Huckins and others (1990) found the measured concentration factors for the compounds studied determined by use of the solvent-filled devices were one to two orders of magnitude smaller than the bioconcentration factors reported in the literature. This may indicate that organic solvents are not valid surrogates for biologic lipids, and(or) that the rate of solvent diffusion out of the sampling device is great enough to prohibit the system from reaching equilibrium over the sampling time period. Additionally, hydrophilic dialysis membranes have been found to be susceptible to degradation by organic solvents and biota.

Researchers at the U.S. Fish and Wildlife Service (FWS) National Fisheries Contaminant Research Center have developed a passive SPMD that addresses some of the problems of earlier designs. Nonporous, low-density polyethylene (or polypropylene) flat tubing is used as a semipermeable membrane. Although this material is referred to as nonporous, it does, in fact, contain small cavities and transient holes of about 5 to 10 Åm diameter. This hydrophobic material is more resistant to degradation by organic solvents and biota than the hydrophilic dialysis membranes used in other samplers, although biofouling on the surface occurs. The replacement of the solvent with lipid makes these samplers more analogous to real fish than earlier designs. This is exemplified by the fact that empirically determined lipid/water partition coefficients, $K_{lw}$ (or lipid concentration factors) are closer to actual bioconcentration factors than published partition coefficients ($K_{oW}$) for most organic contaminants. The larger molecular size of lipid molecules compared to solvent molecules makes the membrane relatively impermeable to the lipid.

The efficacy of the lipid-filled SPMD for concentrating organic contaminants has been tested extensively in laboratory flow-through diluter studies. A few small scale field studies of this technique also have been made. This study is the first large-scale field investigation of the application of lipid-filled SPMDs to monitoring bioavailability of organic contaminants in the environment. This paper briefly describes the SPMD technique and the progress made in this study.

STUDY DESIGN

This study involves the deployment of lipid-filled SPMDs, caged fish, and the collection of indigenous fish in the upper Mississippi River. All field work was carried out by FWS personnel, and was timed to coincide with the U.S. Geological Survey (USGS) Upper Mississippi River study. SPMDs and caged fish were deployed at three sites and samples were collected after 28 days. Indigenous fish were collected 57 days after deployment of the SPMDs.

Initial preparation of SPMD and fish samples was done by FWS personnel. SPMDs were back-dialyzed into hexane and concentrated to 1 mL by rotoevapora-
Fish were dissected in the field to remove their livers and then frozen until ready for further processing. Whole-fish samples were homogenized by FWS personnel, frozen, and sent to the USGS laboratory in Arvada, Colo. Fish-tissue samples were prepared for analysis by extraction with methylene chloride, gel permeation chromatography (GPC), concentration in Kuderna-Danish glassware, and dry nitrogen evaporation. Analysis of sample extracts was performed by gas chromatography/negative chemical ionization/mass spectroscopy (GC/NCI/MS).

**STUDY OBJECTIVES**

This study has several objectives, each of which is specific to the various organizations involved. The primary objective for FWS researchers is to evaluate the efficacy of lipid-filled SPMDs for monitoring the bioavailability of organic contaminants under field conditions. The USGS is interested in assessing the bioavailability of various lipophilic organic contaminants in the Upper Mississippi River. Additionally, the USGS is investigating the partitioning of organic contaminants among SPMDs, fish, suspended silt, colloids, bed sediments, and the aqueous phase.

We hypothesize that, although certain organic compounds will be found in the aqueous phase and in the SPMDs, only their metabolites will be found in the fish. The degree to which SPMDs indicate the bioavailability of these compounds will be assessed quantitatively by comparing lipid concentration factors calculated from SPMD and aqueous concentrations to published bioconcentration factors.

**PROJECT STATUS**

Field sampling has been completed by FWS personnel. SPMD samples have been back-dialyzed, concentrated, and sent to the USGS laboratory. Dialy-sates have been further concentrated and analyzed by GC/NCI/MS. All SPMD data have been tabulated. The presence of the following compounds has been confirmed at quantifiable levels in some or all of the samples from the SPMDs:

- pentachlorobenzene
- hexachlorobenzene
- pentachloroanisole
- dacthal (DCPA)
- trifluralin
- lindane
- heptachlorepoxide
- cis- and trans-chlordane (mostly his-)
- cis- and trans-nonachlor (mostly trans), and
tetra-, penta-, hexa-, hepta-, octa-, and nonachloro-
biphenyls.

All fish samples were collected, homogenized, frozen, and sent to the USGS laboratory by FWS personnel. A fish-tissue extraction protocol has been developed. Initial experiments on the column-extraction procedure showed that post-extraction tissue contained negligible residues of the target compounds. GPC experiments showed good chromatographic separation of lipid and target compounds. With the exception of three problematic compounds (DDD, DDE, and DDT), recoveries for the standard compounds quantitated based on isodrin ranged from 60 to 167 percent; the average recovery was 99 percent. The fish-tissue samples were extracted and have been analyzed by GC/NCI/MS. The fish tissue data are currently being correlated for comparison with the SPMD data.

**REFERENCES**


Measurement of Concentrations of Alachlor and Its Ethanesulfonic Acid Metabolite in Water by Solid-Phase Extraction and Enzyme-Linked Immunosorbent Assay

By Diana S. Aga¹, E. Michael Thurman¹, and Michael L. Pomes¹

Abstract

Solid-phase extraction (SPE) and enzyme-linked immunosorbent assay (ELISA) were combined for the trace analysis of 2-chloro-2',6'-diethyl-N-(methoxymethyl)acetanilide (alachlor) and 2-[(2,6-diethylphenyl)(methoxymethyl)amino]-2-oxoethanesulfonic acid (ESA, a major soil metabolite of alachlor). The anti-alachlor antibody reacted not only with alachlor but also with ESA, which produced false-positive immunoassay detections of alachlor in natural water samples. The combination of SPE with ELISA effectively separates and determines both parent and metabolite compounds; thus, the same antibody may be used for two ELISA methods. Alachlor and ESA were isolated from water by SPE on C18 resin and were eluted sequentially with ethyl acetate and methanol. The separation involves the difference in solubility of the ionic sulfonic acid in ethyl acetate and methanol. The SPE-ELISA method has a detection limit of 0.01 µg/L (micrograms per liter) for alachlor and 0.05 µg/L for ESA with a precision of ±10 percent. Analyses of surface-water and ground-water samples were confirmed by high-performance liquid chromatography with photodiode-array detection and gas chromatography/mass spectrometry. Results showed widespread presence of ESA in surface water and ground water of the midwestern United States in concentrations of 0.10 to greater than 10 µg/L.

INTRODUCTION

Solid-phase extraction (SPE) and enzyme-linked immunosorbent assay (ELISA) are two analytical techniques that recently have found wide application in environmental chemistry. For example, ELISA has been applied to the analysis of herbicide residues in soil and water (Bushway and others, 1988; Vanderlaan and others, 1988; Schlaeppi and others, 1989; Feng and others, 1990a, 1990b; Thurman and others, 1990; Goh and others, 1991; Van-Emon and Lopez-Avila, 1992). ELISA is a sensitive, fast, and cost-effective technique that can be conducted both in the laboratory and in the field. However, most of the applications of ELISA are limited to the screening of samples in a complex environmental matrix, which may lead to false-positive detections of the target analytes (Feng and others, 1990a, 1990b; Baker and others, 1993). Less commonly, false-negative detections are observed when the detection limit of the assay is reached. Furthermore, the immunoassay performance can be affected substantially not only by cross-reacting compounds, but also by matrix components that interfere with the assay detection system and the antibody-antigen interactions.

SPE is used extensively as a clean-up procedure for clinical and environmental samples (Morris and Ruthann, 1988; Tippins, 1988). In contrast to ELISA, which can detect known substances, SPE can separate unknown substances by mechanism similar to those of high-pressure liquid chromatography (Morris and Ruthann, 1988). The complimentary features of these two techniques may be combined for a selective and

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sensitive analytical method that is analogous to a chromatographic separation, where the SPE cartridge is the column and ELISA is the detector. With properly designed SPE procedures, the reliability of the immunoassay may be greatly enhanced by separating closely related compounds and reducing false-positive detections. Moreover, because SPE is also a preconcentration technique, the sensitivity of the ELISA may be increased by several orders of magnitude. Because SPE is easily automated for water analysis (Castellani and others, 1990; Meyer and others, 1993), the reproducibility and speed of immunoassay is not compromised. In addition, cross reactivity, which commonly is viewed as a major drawback for quantitative immunoassay, can be a positive aspect of ELISA by using the same antibody to quantitate a cross-reacting compound after the compounds have been separated by SPE.

Alachlor, a widely used herbicide in the midwestern United States, and its relatively persistent and very mobile ethanesulfonic acid metabolite, ESA (Baker and others, 1993), are important target compounds for the development of a sensitive assay that combines SPE and ELISA. The high frequency of false-positive detections observed in the ELISA screening kits for alachlor have been attributed to the significant cross reactivity of the ESA metabolite towards the anti-alachlor antibody (Macomber and others, 1992; Baker and others, 1993). The specific objectives of the study reported herein were to (1) understand the principles involved in separating parent herbicides and ionic metabolites by SPE, (2) couple SPE and ELISA for analysis of alachlor and ESA, (3) apply the method on samples of surface water and ground water and compare the results with gas chromatography/mass spectrometry (GC/MS) and high-performance liquid chromatography with photodiode-array detection (HPLC/PDA).

METHODS

Solid-Phase Extraction Procedure

The SPE procedure was automated with a Millipore Workstation. The SPE cartridges containing 360 mg of 40-mm C18-bonded silica were washed sequentially with 2 mL of methanol, 6 mL of ethyl acetate, 2 mL of methanol, and 2 mL of distilled water. One hundred (100) mL of sample were passed through the cartridge at a flow rate of 10 mL/min. The cartridge was eluted with 3 mL of ethyl acetate, followed by a transfer step to remove the ethyl acetate (top layer) containing the alachlor from the residual water (bottom layer) in the eluate. Then, the cartridge was eluted with methanol to remove the ESA, which was collected in a separate test tube. Both ethyl-acetate and methanol extracts were evaporated to dryness under nitrogen at 45°C (degrees Celsius). The ethyl-acetate extracts were reconstituted with 1 mL of 20 percent methanol-water mixture, and the methanol extracts were reconstituted with 5 mL of water for analysis by ELISA (fig. 1).

The preparation of samples for GC/MS and HPLC analysis was performed in a similar SPE procedure. The ethyl-acetate extracts were spiked with phenanthrene-d10, which was used as the external standard for quantitation, and the sample volume was reduced to about 100 µL for the analysis of alachlor by GC/MS. The methanol extracts for HPLC analysis were evaporated to dryness and redissolved in 100 µL of 10 mM phosphate buffer/methanol (20/80) mixture.

Enzyme-Linked Immunosorbent Assay Procedure

ELISA kits from two different manufacturers were used to analyze each solid-phase eluate. One type of alachlor ELISA kit had antibodies coated on the wells of the microtiter plate, and the other type of alachlor ELISA kit had antibodies covalently attached to magnetic particles. Each extracted sample was analyzed in duplicate. For the microtiter plate-based ELISA kit, 80 µL of sample and 80 µL of hapten-enzyme conjugate were mixed in the well, and the mixture was incubated at 30 °C in an orbital shaker (200 revolutions per minute). After 1 hour, the plate was rinsed five times with deionized water, and excess water was removed. One hundred sixty (160) mL of color reagent (1:1 mixture of hydrogen peroxide and 3,3',5,5'-tetramethylbenzidine or TMB) were added, and the color developed for 30 minutes. Then, the stop solution (40 µL, 2 M sulfuric acid) was added. Optical densities were read on a microplate reader using computer software. The alachlor concentration in the samples were calculated by interpolation from four
Alachlor and sulfonic acid metabolite (100-milliliter sample)

SPE C18 cartridge

1. Effluent to waste
2. Elute with 3 milliliters of ethyl acetate (contains alachlor)
3. Elute with 2 milliliters of methanol (contains ethanesulfonic acid and oxo-acetic acid metabolites)

(a) Analysis by ELISA: evaporate to dryness, then reconstitute with 1 milliliter of 20 percent methanol-water mixture.
(b) Analysis by GC/MS: spike with phenanthrene-d10 and evaporate to dryness.

(a) Analysis by ELISA: evaporate to dryness, then reconstitute with 5 milliliters of distilled water.
(b) Analysis by HPLC: spike with metribuzin and evaporate to dryness, then reconstitute with 100 microliters of 20/80 buffer/methanol mixture.

Figure 1. Flow chart for illustrating analytical method using solid-phase extraction (SPE) and enzyme-linked immunosorbent assay (ELISA), gas chromatography/mass spectrometry (GC/MS), or high-performance liquid chromatography (HPLC).

For the magnetic particle-based ELISA kits, 250 μL of sample were mixed with 250 μL of hapten-enzyme conjugate and 500 μL of paramagnetic particles. This mixture was incubated for 30 minutes at room temperature, and a strong magnetic field was applied. The excess reagent was removed. Then, 500 μL of color reagent were added, and the mixture was incubated for 20 minutes at room temperature (25 °C), followed by addition of the stop solution (500 μL).

The optical densities were read using a photometric analyzer, and concentrations were calculated from logarithmically transformed data with the same set of alachlor standards used for the microtiter plate-based ELISA. ESA analysis was performed using the alachlor magnetic particle-based ELISA that was calibrated with ESA standards at concentrations of 20, 5.0, 1.0, and 0 μg/L.

Analysis by Gas Chromatography/Mass Spectrometry

Operating conditions for the GC/MS analysis of alachlor were identical to those described by Thurman and others (1990). The detector was operated in a selected-ion-monitoring (SIM) mode, and confirmation was based on the presence of the molecular-ion peak, two confirming ions (with area counts of ±20 percent) and a retention time match of ±0.2 percent relative to phenanthrene-d10. The ratio of the base-peak ion of alachlor and the 188-amu (atomic mass unit) ion of phenanthrene-d10 were used to construct the calibration curve. A 12-m fused-silica capillary column of methylsilicone with a film thickness of 0.33 μm and 0.2 mm inside diameter was used for separation. Helium was used as the carrier gas with a flow rate of 1 mL/min and a head pressure of 35 kPa. The samples were injected in the splitless mode by an auto-injector. The column temperature was held at 50 °C for 1 minute, then increased at 6 °C.
per minute to 250 °C and held at this temperature for 10 minutes. Injector temperature was 280 °C.

**Analysis by High-Performance Liquid Chromatography**

The HPLC analysis of the methanol extracts for the confirmation of ESA was performed in liquid chromatograph with a photodiode-array (PDA) detector. The HPLC was equipped with a 2.1 x 100 mm narrow bore, reversed-phase column, packed with 5 mm of octadecysilyl. The mobile phase consisted of 38.5-percent HPLC-grade methanol and 61.5-percent 10 mM dibasic sodium phosphate (pH 7 buffer). The flow rate of the mobile phase was 1.2 mm/min. The sample injection volume was 90 μL. ESA was monitored at a wavelength of 200 nm with a 4-nm bandwidth. The reference wavelength was set at 450 nm with a 80-nm band width. To confirm the identity of the ESA, the ultraviolet spectra were scanned from 190 to 400 nm and the spectra matched to standard spectra in an automated library search. A fixed quantity of metribuzin (500 ng) was spiked into each methanol extract to serve as the internal standard for quantitation. A detailed discussion on the HPLC method is presented by Pomes and others (this volume).

**RESULTS AND DISCUSSION**

**Acetanilide Cross-reactivity and Enzyme-linked Immunosorbent Assay Development**

The cross reactivity of the antibodies in the two alachlor ELISA kits with other acetanilides and alachlor metabolites was determined (fig. 2). Cross reactivities were expressed as IC50, which is the concentration of the compound that causes 50-percent inhibition of absorbance, and as the least detectable dose (LDD), which is the concentration at 90-percent inhibition of absorbance. Both ELISA kits were most sensitive for alachlor and had a LDD of 0.07 μg/L and 0.06 μg/L, for the magnetic particle-based and microtiter plate-based ELISA, respectively. The magnetic particle-based ELISA had an IC50 of 0.89 μg/L, whereas the microtiter plate-based ELISA had an IC50 of 0.75 μg/L for alachlor. The compound with the highest cross reactivity was ESA, which had an IC50 of 5.4 μg/L and a LDD of 0.19 μg/L for the magnetic particle-based ELISA, and an IC50 of 1.7 μg/L and a LDD of 0.12 μg/L for the microtiter plate-based ELISA. The oxo-acetic acid (OXA) metabolite of alachlor had an IC50 of 335 μg/L and a LDD of 21 μg/L (magnetic particle-based ELISA) and an IC50 of 66 μg/L and a LDD of 2.7 μg/L (microtiter plate-based ELISA).

The cross reactivity with ESA has caused problems in previous water-quality surveys for alachlor by ELISA because of false-positive detections of alachlor (Macomber and others, 1992; Baker and others, 1993). Furthermore, it has been reported that the ELISA for alachlor does not correlate well with GC/MS and gives more than 10-percent false-positive detection near the detection limit of the assay, from 0.10 to 0.20 μg/L (Feng and others, 1990a, 1990b). This poor correlation has been attributed to the presence of high ESA concentrations as confirmed by liquid chromatography and mass spectrometry (Macomber and others, 1992). ESA and OXA are two major soil metabolites of alachlor (Sharp, 1988); however, only ESA appears to have enough significant cross reactivity to cause interference with ELISA (fig. 2).

Other soil metabolites of alachlor, such as chlorodiethylacetanilide and hydroxydiethylacetanilide, did not show any cross reactivity up to a concentration of 1,000 μg/L. Metolachlor, another major corn herbicide, showed small cross reactivity, with an IC50 of 109 and 27 μg/L for magnetic particle-based and microtiter plate-based ELISA, respectively. This cross-reactivity pattern suggests that the binding of alachlor towards the antibody is greatly affected by the presence of the methoxymethyl side chain. These results are not surprising because the antibodies against alachlor were generated by the use of an alachlor-protein conjugate, formed through the chlorine-bearing carbon of alachlor via a thioether bond (Feng and others, 1990a, 1990b). The thioether may explain the cross reactivity of ESA, which has nearly the same structure as the hapten-protein conjugate used for antibody generation, whereas the OXA does not show any significant cross reactivity despite of the similar structure of the molecule.

**Separation by Solid-Phase Extraction**

The separation of alachlor and ESA was achieved by SPE using a C18 resin. Both compounds adsorbed quantitatively from water onto the C18
Figure 2. Cross-reactivity of antibodies with chloroacetanilide herbicides and alachlor metabolites expressed as the concentration required for 50-percent inhibition (IC50), in micrograms per liter, and in least detectable dose (LDD) at 90-percent inhibition. The first value is for the magnetic particle-based ELISA and the second value is for the microtiter plate-based ELISA.

cartridge (table 1). Alachlor has a large capacity on the C18 resin; more than 7 L of sample could pass through the cartridge before a 10-percent breakthrough was observed. In contrast, ESA has considerably less capacity; a 10-percent breakthrough and a 100-percent breakthrough were observed after 175 mL and 750 mL of sample, respectively, had passed through the cartridge (table 1). This difference in capacity is caused by the higher water solubility of ESA compared to that of alachlor. Likewise, OXA has a relatively small capacity on the C18 resin, with a 10-percent breakthrough beginning at 150 mL and a 100-percent breakthrough observed after 750 mL. A more soluble herbicide, 2,4-dichlorophenoxyacetic acid (2,4-D), also was examined. It was found that 2,4-D had a very small capacity for sorption, with a 10-percent breakthrough observed after only 10 mL of sample had passed through the cartridge and a 100-percent breakthrough observed after 90 mL (table 1). These results suggest that the isolation of ionic compounds on C18 resin is possible, but this isolation

<table>
<thead>
<tr>
<th>Compound</th>
<th>10-percent breakthrough</th>
<th>100 percent breakthrough</th>
</tr>
</thead>
<tbody>
<tr>
<td>alachlor</td>
<td>&gt;7,000</td>
<td>---</td>
</tr>
<tr>
<td>ethanesulfonic acid metabolite (ESA)</td>
<td>175</td>
<td>750</td>
</tr>
<tr>
<td>oxo-acetic acid metabolite (OXA)</td>
<td>150</td>
<td>750</td>
</tr>
<tr>
<td>2,4-dichlorophenoxyacetic acid (2,4-D)</td>
<td>10</td>
<td>90</td>
</tr>
</tbody>
</table>

Table 1. Breakthrough capacity of alachlor and other ionic compounds on C18 cartridges
[capacity in mL; > , greater than. ---, not measured]
technique is quite sensitive to the aqueous solubility of the analyte. Thurman and others (1978) reported that ionic character was critical in the sorption of organic acids onto a macroporous acrylic resin and was a function of chain length. The same concept applies to the isolation of ionic metabolites on C₁₈ resin because both isolations involve hydrophobic interactions.

The separation of ESA and alachlor occurs in the elution step. Alachlor is eluted with ethyl acetate without removal of ESA (table 2). ESA then is eluted with methanol; elution efficiency is greater than or equal to 90 percent. HPLC data showed that OXA also elutes with methanol (Pomes and others, this volume), but because OXA has almost no cross reactivity with the ELISA kits, it does not interfere with the analysis of ESA by ELISA.

### Combining Solid-Phase Extraction and Enzyme-linked Immunosorbent Assay

The SPE-ELISA method for ESA is shown in figure 1. A 100-mL sample was passed through the C₁₈ cartridge, and the alachlor and ESA were quantitatively sorbed to the resin. The alachlor was eluted with ethyl acetate, which, in turn, was analyzed by ELISA using the magnetic particle-based alachlor assay and then verified by GC/MS. The ESA was eluted with methanol, then methanol was evaporated to dryness, and the ESA was reconstituted with water. This mixture was analyzed by ELISA using the magnetic particle-based alachlor assay but calibrated with ESA standards and then verified by HPLC. It should be noted that solvent exchange of the organic solvent to an aqueous medium was performed prior to ELISA.

The method worked well with fortified water samples (table 2). Alachlor recovery from the ethyl-acetate extract was 100 percent and from the methanol extract was 0 percent, whereas 90 to 99 percent of the ESA was recovered from the methanol extract and none was recovered from the ethyl-acetate extract. Thus, the separation technique allowed for good quantitation of ESA by immunoassay. The calibration curve for ESA was linear for concentrations of 1.0 to 20 μg/L. Because SPE preconcentrates the sample, the detection limit can be as low as 0.05 μg/L when a 100-mL sample is used for SPE and the dried extract is diluted to 5 mL water.

### Table 2. Recovery of alachlor and ethanesulfonic acid (ESA) metabolite from a C₁₈ resin by sequential elution with ethyl acetate and methanol by SPE

<table>
<thead>
<tr>
<th>Concentrations in fortified distilled water</th>
<th>Percentage of alachlor recovered in ethyl acetate</th>
<th>Percentage of ESA recovered in methanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. 0 μg/L alachlor + 0.20 μg/L ESA</td>
<td>0</td>
<td>92</td>
</tr>
<tr>
<td>B. 0.050 μg/L alachlor + 0.10 μg/L ESA</td>
<td>100</td>
<td>97</td>
</tr>
<tr>
<td>C. 0.10 μg/L alachlor + 0.050 μg/L ESA</td>
<td>97</td>
<td>99</td>
</tr>
<tr>
<td>D. 0.025 μg/L alachlor + 0.025 μg/L ESA</td>
<td>105</td>
<td>90</td>
</tr>
<tr>
<td>E. 0.20 μg/L alachlor + 0.0 μg/L ESA</td>
<td>98</td>
<td>0</td>
</tr>
</tbody>
</table>

The automated workstation combined with SPE performs as a liquid chromatograph with a fraction collector by pumping the sample through the cartridge, separating the compounds by sequential elution, and collecting the fractions for analysis by immunoassay, GC/MS, or HPLC. The automated SPE procedure is capable of reproducing the separation within ±10 percent.

The ability of SPE to separate alachlor and ESA was demonstrated on ground-water samples from various locations. The presence of both alachlor and ESA in the ground-water samples resulted in an overestimation of alachlor when water samples were analyzed directly by ELISA. The discrepancy between the amount of alachlor measured by GC/MS and that measured by ELISA was proportional to the amount of ESA in the sample. However, when the water samples were passed through SPE and the ethyl-acetate eluate was analyzed for alachlor by ELISA, the concentration of alachlor agreed with that obtained by GC/MS. In addition, analysis of the methanol eluates by ELISA showed high concentrations of ESA whenever there was a discrepancy between alachlor concentrations measured by ELISA and GC/MS. This indicates further that ESA, which caused the false alachlor concentration in ELISA, was recovered in the methanol extract and not in the ethyl-acetate extract. These results suggest that the SPE-ELISA method is quite effective for the separation and analysis of alachlor and ESA.

The correlation of HPLC and SPE-ELISA for 22 surface-water samples from reservoirs in the midwestern United States is shown in figure 3A. The correlation coefficient (r) was 0.93, and the slope of 0.69 demonstrates that the two methods correlate quite well and that HPLC concentrations were generally smaller. The smaller ESA concentrations determined
by HPLC analysis may be attributed to high concentrations of humic and fulvic acids that were coextracted in the methanol fraction. ESA concentrations of less than 0.10 µg/L are difficult to measure using HPLC because natural organic substances that are recovered in the methanol fraction produce a large background signal in the HPLC. However, ground-water samples were comparatively easy to analyze by HPLC because of the relatively small quantities of humic and fulvic acids in the samples, which produce clean extracts. Figure 3B shows the high correlation between ESA concentrations determined by ELISA and by HPLC (r = 0.97). The ESA concentration in water samples from the various reservoirs ranged from less than 0.10 µg/L to more than 10 µg/L. Further studies are underway to understand the fate and transport of ESA in the soil and in the aquatic environment.

SUMMARY

The coupling of SPE and ELISA results in a reproducible immunoassay method for the trace analysis of alachlor and its major soil metabolite, ESA, in ground water and surface water. The results are comparable to both GC/MS and HPLC results, for alachlor and ESA, respectively. The procedure uses SPE to isolate and concentrate the herbicide and metabolite and uses sequential elution with ethyl acetate and methanol to separate the two compounds. The method is sensitive with a quantitation limit of 0.01 µg/L for alachlor and 0.05 µg/L for ESA, and a precision of ±10 percent.

REFERENCES


Isocratic Separation of Alachlor Ethanesulfonic Acid, Alachlor Oxoacetic Acid, and Hydroxyatrazine by Reversed-Phase Liquid Chromatography

By Michael L. Pomes¹, Douglas F. Holub¹, Diana S. Aga,¹ and E.M. Thurman¹

Abstract

The polar nature of two alachlor metabolites, alachlor ethanesulfonic acid and alachlor oxoacetic acid, makes their detection by gas chromatography/mass spectrometry impossible without derivatization. Enzyme-linked immunosorbent-assay techniques cannot distinguish alachlor metabolites from alachlor; thus, reversed-phase high-performance liquid chromatography with photodiode-array detection is required for the separation and spectral detection of these analytes. Use of an isocratic, methanol/10 millimolar sodium phosphate dibasic buffer mixture as the mobile phase with reversed-phase (C-18) high-performance liquid chromatography allows for the separation and quantification of alachlor ethanesulfonic acid, alachlor oxoacetic acid, and hydroxyatrazine at concentrations greater than or equal to 0.10 micrograms per liter in 100-milliliter water samples. The buffer in the methanol mixture provides cations that ion pair with the alachlor metabolite anions to decrease polarity and promote nonpolar interactions between the analytes and the reversed-phase column. Enhanced chromatographic resolution results from injecting samples in a matrix that contains less methanol than the mobile phase. The disparity between the methanol content of the sample matrix and the mobile phase focuses the analytes at the head of the chromatographic column to produce sharper peaks because the analytes are less soluble in the sample matrix than in the mobile phase. Results by reversed-phase high-performance liquid chromatography show that one can detect alachlor ethanesulfonic acid in surface-water, along with lesser concentrations of alachlor oxoacetic acid and hydroxyatrazine.

INTRODUCTION

While developing an enzyme-linked immunosorbent assay (ELISA) for alachlor, Feng and others (1990) reported that their technique produced false positive results. The ELISA tested positive for alachlor, but the presence of alachlor could not be confirmed by gas chromatography/mass spectrometry (GC/MS). Recently, one of the alachlor metabolites, 2-[(2,6-diethylphenyl)(methoxymethyl)amino]-2-oxoethanesulfonic acid (ESA), analyzed by Feng and others (1990), has been identified as the source of many alachlor ELISA false positives detected in ground-water samples (Macomber and others, 1992; Baker and others, 1993).

ESA exists as an anion in solution and is too polar to be detected by GC/MS techniques without derivitization. ESA can be extracted from water samples using solid-phase extraction (SPE) cartridges, but the polarity of ESA requires elution of the cartridges with methanol, a polar solvent (Macomber and others, 1992; Aga and Thurman, 1994). Methanol also is used in the mobile phase for the analysis of ESA by high-performance liquid chromatography (HPLC) (Macomber and others, 1992). This paper addresses the HPLC separation of ESA oxoacetic acid [(2,6-diethylphenyl)-(methoxymethyl)amino]oxoacetic acid] (another soil metabolite of alachlor) (Feng and others, 1990), and hydroxyatrazine in surface-water samples. Like the alachlor metabolites, hydroxyatrazine is relatively polar, can not be analyzed by GC/MS techniques without derivitization, and elutes from the

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PREVIOUS WORK

ESA and Oxoacetic Acid

Macomber and others (1992) reported reversed-phase chromatography techniques for the analysis of ESA and oxoacetic acid using a C-18 column. Before analysis, 1 mL sodium phosphate dibasic buffer was added to the 1-mL methanol extract containing the analytes and injected on the HPLC with a 50-μL injection. The mobile phase used to separate ESA consisted of a 50/50 (v/v; volume to volume) mixture of methanol and 50 mM (millimolar) sodium phosphate dibasic (Na₂HPO₄) pH 7.0 buffer. The buffer allowed sodium (Na) cations to pair with the analyte anions to produce neutral compounds that interact with the C-18 column. ESA and oxoacetic acid were detected with a UV detector set at wavelength of 205 nm.

Hydroxyatrazine

Various chromatographic techniques have been used for the detection and quantification of hydroxyatrazine. Rustum and others (1990), Qain and others (1991), and Wang and others (1992) have used reversed-phase chromatography with C-18 columns to determine concentrations of hydroxyatrazine in soil extracts. Vermeulen and others (1982) used a reversed phase C-8 column for analyzing atrazine and selected metabolites because they found some of the metabolites too polar to be retained on C-18 columns.

Mobile phases used to analyze hydroxyatrazine ranged from gradient elutions to combinations of acetonitrile and buffers or water at different pH's. Wang and others (1992) used a 50/50 acetonitrile/water mobile phase containing 3.18 mM hydrochloric acid (HCl) to give a pH of 2.5. Rustum and others (1990) used a gradient elution consisting of 0.01 M potassium phosphate dibasic (K₂HPO₄) (pH 2.0 stabilized with phosphoric acid) and acetonitrile (5 percent for 0 to 10 minutes, 20 percent for 10 to 15 minutes, 30 percent for 15 to 20 minutes, and 70 percent for 20 to 35 minutes). Qain and others (1991) also used a 50/50 acetonitrile/water mixture but added 0.020 M n-heptane sulfonic acid (pH of 2.8) and phosphoric acid to perform ion-pair reverse-phase liquid chromatography. Vermeulen and others (1982) used a mobile phase consisting of 40/60 methanol/water with 50 mM ammonium acetate dissolved in each component to produce a solution pH of 7.4.

Detection strategies used to identify hydroxyatrazine range from single wavelength detection to use of photodiode array (PDA) detectors. PDA detectors consist of a ultraviolet/visible lamp (UV/VIS), diffraction grating, detector cell, and a silicon-chip array with slots dedicated to individual wavelengths (Harris, 1991). Radiant energy striking a particular slot causes that part of the chip to partially discharge. During recharging, a computer monitors the amount of energy required to recharge the entire array. Regions of the spectrum where maximum absorbance occurs correspond to the parts of the diode array that needed the most recharging. Rustum and others (1990) used a wavelength of 230 nm for the detection of hydroxyatrazine with deethylatrazine, desopropylatrazine, deethylydroxyatrazine, and desopropylhydroxyatrazine. Qain and others (1990) used a PDA detector that scanned the absorption spectrum of each peak between 190 and 300 nm. They reported the maximum ultraviolet absorbance of hydroxyatrazine to be 215 nm. Vermeulen and others (1982) used a wavelength of 220 nm for the detection of hydroxyatrazine with deethylatrazine, desopropylatrazine, deethylydroxyatrazine, and desopropylhydroxyatrazine. Finally, Wang and others (1992) used a wavelength of 254 nm for the detection and quantification of atrazine and hydroxyatrazine.

METHODS

Solvents and Standards

Solvents used during the course of this study included ethyl acetate and HPLC grade methanol. Alachlor ethanesulfonic acid, alachlor oxoacetic acid and hydroxyatrazine were prepared as 1-mg/mL (milligram per milliter) stock solutions in HPLC grade methanol and stored in a freezer.

Apparatus and Instrumentation

Syringes used for the preparation of standards and the spiking of appropriate volumes of water included 10-μL and 100-μL gas-tight syringes.

Automated solid-phase extraction of the analytes from water was accomplished with the automated workstation using C-18 SPE cartridges. Volume reduction of the eluted herbicide samples was accomplished with nitrogen evaporation. Analysis and quantitation of the herbicide metabolites in this study was completed with a liquid chromatograph and controller. A 3-μm particle size C-18 column, 100 mm x 4.6 mm, was used in the HPLC for separation. The autosampler on the HPLC used a 250-μL syringe, and detection and spectral analysis of analytes used a PDA. The PDA detector allowed the simultaneous monitoring of eight separate wavelengths and the scanning of spectra between 190 and 600 nm.

**Extraction and Analysis**

The analytes under consideration for this study were extracted from 100-mL sample volumes using C-18 SPE cartridges and the automated workstation. Details of the extraction process are discussed in Aga and Thurman (1994). The final step of the process consisted of separate elutions of ethyl acetate and methanol. The cartridge was eluted with 3.0 mL ethyl acetate to remove the less polar compounds such as atrazine and alachlor. This fraction then was prepared for GC/MS analysis. The SPE cartridge was eluted with 5.0 mL of methanol into a centrifuge tube. Because of their polarity, hydroxyatrazine and the alachlor metabolites remained on the cartridge during the ethyl acetate elution but were removed by the more polar methanol. The 5.0-mL methanol extract was spiked with metribuzin (4-amino-6-(1,1-dimethyl-ethyl)-3-(methylthio)-1,2,4-triazin-5(4H)-one), the internal standard, then evaporated to dryness with a nitrogen stream at 45 °C. One hundred microliters of a 20/80 methanol/10 mM Na₂HPO₄ buffer mixture was added to the centrifuge tube, and the tube was vortexed. The sample then was transferred to a crimp-capped microvial for analysis on the HPLC.

The following operating conditions were used to detect and quantify the analytes of interest in this study. The mobile phase consisted of a 31.5/68.5 methanol/10 mM Na₂HPO₄ buffer mixture. The mobile phase, heated to a temperature of 60 °C, flowed through the standard bore C-18 column at 1.20 mL/min. The detector wavelength was set at 200 nm with a 4-nm bandwidth; the reference wavelength was set to 450 nm with a 80-nm bandwidth. Finally, an injection volume of 90 μL was used to introduce samples to the HPLC. Use of the 90-μL injection in conjunction with a 100-mL sample volume allowed the separation and detection of alachlor ethanesulfonic acid, alachlor oxoacetic acid, and hydroxyatrazine at concentrations greater than or equal to 0.10 μg/L using 100-mL water samples.

The last step in the HPLC analysis involved the identification and quantitation of the herbicide metabolite analytes in the water sample. Two options in the HPLC operating software were used for the identification. The first, a peak purity check, measured the spectrum on the upslope of the peak, top of peak, and downslope of the peak. If the peak consisted of coeluting analytes, different, nonmatching spectra would be collected. If a peak consisted of one analyte, the upslope, top, and downslope spectra would all match; therefore, the peak was considered pure. The second option, an automated library search, matched analyte spectra against standards stored in the library. Analyte areas and peak heights were quantified relative to metribuzin.

**DISCUSSION**

The UV spectra and the chemical structures of the analytes of interest in this study are illustrated in figure 1. Of the three compounds and internal standard, both ESA and oxoacetic acid had maximum UV absorbances of 196 nm. Because ESA and oxoacetic acid had similar UV spectra, a wavelength of 200 nm was used as the detector wavelength as opposed to the 205-nm wavelength used by Macomber and others (1992). The choice of 200 nm, which is less than the UV cutoff of 205 nm for methanol hence necessitated zeroing the detector with a 100-percent methanol mobile phase before any analysis was completed. Hydroxyatrazine and metribuzin had UV maxima greater than 200 nm, and the wavelengths corresponding to their maximum absorbances could be monitored with a diode-array detector. However, only the 200-nm wavelength was monitored because the peak purity and automated library search routines did not function properly if more than one wavelength was monitored.

Other changes made to the operating conditions originally used by Macomber and others (1992) arose from addition of o xoacetic acid as an analyte. In chromatographs completed at ambient temperatures, oxoacetic acid standards had two peaks rather than one (fig. 2A). Having two peaks in a standard rather than
Figure 1. Ultraviolet (UV) maxima and chemical structures of alachlor ethanesulfonic acid, alachlor oxoacetic acid, hydroxyatrazine, and metribuzin.

one may indicate a contaminant in the standard. Heating the mobile phase caused the two peaks to blend until essentially one peak occurred at temperatures greater than 50 °C (fig. 2B). The presence of a contaminant in the oxoacetic acid standard was discounted by the fact that a pure peak was indicated by the peak purity test at temperatures greater than 50 °C. Apparently, some equilibrium must exist for oxoacetic acid between the two isomers so that two peaks occurred at ambient temperatures, and one peak occurred at higher temperatures.
Figure 2. Chromatographs of oxoacetate acid at (A) 27 degrees Celsius showing two peaks and (B) 55 degrees Celsius showing a single peak. Oxoacetic acid standard mixed in sample matrix consisting of 50/50 mixture of methanol and 20 millimolar sodium phosphate dibasic pH 7.0 buffer. Mobile phase consists of a 44/56 mixture of methanol and 20 millimolar sodium phosphate dibasic pH 7.0 buffer flowing at a rate of 1.2 milliliters per minute through the column.
A rotational isomer of oxoacetic acid may be responsible for the second peak observed at ambient temperatures (Drew Kline, Monsanto, oral commun., 1993). Because of oxoacetic acid rotational isomers, the mobile phase was heated to 60 °C. Although one oxoacetic acid peak was evident at 60 °C, the peak had a width exceeding 1 minute when measured along the baseline. Additional work was undertaken to decrease peak width. The oxoacetic acid peak width decreased and peak height increased when the concentration of Na₂HPO₄ was decreased in the mobile phase and sample matrix. Specifically, peak height nearly doubled when the concentration of Na₂HPO₄ was decreased from 20 to 10 mM. Use of the heated mobile phase and decreased buffer concentration enhanced the ability to detect oxoacetic acid.

Two aspects involving the width of chromatographic peaks became apparent in deciding the appropriate conditions for the analysis of ESA, oxoacetic acid, and hydroxyatrazine. Peak width could be broadened noticeably if the methanol part of the sample matrix exceeded that of the mobile phase. Alternately, peak width could be narrowed, and peak height noticeably increased if the methanol part of the mobile phase exceeded that of the sample matrix. In the latter case, increased chromatographic resolution resulted from injecting samples in a matrix that contained proportionally less methanol than did the mobile phase. The disparity between the methanol content of the sample matrix and the mobile phase focused the analytes at the head of the chromatographic column to produce sharper peaks because the analytes were less soluble in the sample matrix than in the mobile phase. The chromatographic conditions used for the set of analytes under discussion used a sample matrix consisting of 20 percent methanol and a mobile phase consisting of 38.5 percent methanol.

The order of elution of the analytes in a 25 ng/μL standard mixture is illustrated in figure 3A. Oxoacetic acid has an average retention time of 2.81 minutes; hydroxyatrazine, 3.14 minutes; ESA, 3.40 minutes; and metribuzin, 4.71 minutes. Results by reversed-phase high-performance liquid chromatography show that one can detect alachlor ethanesulfonic acid in surface water, along with lesser concentrations of alachlor oxoacetic acid and hydroxyatrazine. Chromatograms of surface-water samples with positive detections of oxoacetic acid, ESA, and hydroxyatrazine are illustrated in figures 3B and 3C. Additionally, the chromatograms of the surface-water samples share large peaks that elute during the early part of the analysis. These large peaks probably are due to the humic material present in surface water. Humic material accumulates on the SPE cartridges and is partially removed from the cartridge with methanol (Mills and Thurman, 1992) to the extent that many of the sample extracts are yellow-colored prior to injection on the HPLC. The presence of humic material in these extraction of oxoacetic acid, hydroxyatrazine, and ESA by causing elevated baselines. More work needs to be done to minimize the effect of humic material using reversed-phase HPLC.

**SUMMARY**

Hydroxyatrazine was isolated by solid-phase extraction and methanol elution of two polar alachlor metabolites, oxoacetic acid and ESA. The polarity of these metabolites requires that the buffer used in the mobile phase for HPLC analysis must contain cations to pair with the anionic alachlor metabolites. Using a wavelength of 200 nm (closer to the UV maxima for oxoacetic acid and ESA) and an injection volume of 90 μL, analyte concentrations greater than or equal to 0.10 μg/L were detected and quantified from 100-mL water samples. Chromatography of oxoacetic acid was improved by heating the mobile phase to 60 °C to assure that only one oxoacetic acid peak was detected, and decreasing the concentration of the buffer to 10 mM greatly increased peak height. Additional chromatographic resolution was achieved by injecting a sample matrix containing proportionally less methanol than the mobile phase. The disparity between the methanol content of the sample matrix and the mobile phase focuses the analytes at the head of the chromatographic column to produce sharper peaks because the analytes are less soluble in the sample matrix than in the mobile phase. Results by reversed-phase HPLC show that one can detect alachlor ethanesulfonic acid in surface water, along with lesser concentrations of alachlor oxoacetic acid and hydroxyatrazine. However, the presence of humic material in surface-water samples, isolated by solid-phase extraction and eluted into the extract with methanol, poses a potential interference to the method.
Figure 3. Chromatographs of (A) 25 nanograms per microliter standard mixture of oxoacetic acid hydroxyatrazine, ESA, and metribuzin, 10-microliter injection, (B) surface-water sample showing positive identifications of oxoacetic acid and ESA, and (C) surface-water sample showing positive identification of hydroxyatrazine.
REFERENCES


Use of $^{15}\text{N}$ to Trace Movement of Nitrogen Fertilizer at a Field Plot

By Dale W. Blevins¹, Donald H. Wilkison¹, Steven R. Silva², and Brian P. Kelly¹

Abstract

A simplified, lower-cost technique for preparation of water samples for nitrogen isotope ($\delta^{15}\text{N}$) analysis of nitrate ($\text{NO}_3$) is being tested. Anion exchange resins were used to concentrate nitrate in the field and samples were prepared for $\delta^{15}\text{N}$ - NO$_3$ (ratio of $^{15}\text{N}$ to $^{14}\text{N}$ in NO$_3$, relative to atmospheric N, expressed in per mil) analysis using a modification of the Dumas combustion method. Initial test results of the $\delta^{15}\text{N}$ - NO$_3$ technique indicate that a precision of 0.05 per mil can be achieved. More than 99 percent of nitrate in solution is sorbed onto the resins. Hydrochloric acid was used to elute 95 to 100 percent of the nitrate from the resins. Chloride and organic molecules can interfere with $\delta^{15}\text{N}$ - NO$_3$ values, but not at concentrations detected at the field plot.

The $^{15}\text{N}$-labeled fertilizer was applied to a 0.1-acre field plot in May 1992 to determine the quantity of nitrogen fertilizer reaching ground water. Twenty-two percent of the labeled fertilizer was removed from the plot in harvested grain. Soil-gas analyses indicated no significant denitrification of the applied fertilizer. Labeled fertilizer accounted for 34 percent of the nitrate in runoff in the first storm after application. Small quantities of labeled fertilizer were detected 1.5 feet below ground surface 1 month after application, but evapotranspiration prevented further downward movement until November 1992. Labeled fertilizer was detected in shallow wells within 6 days of the first recharge event in November 1992.

The $\delta^{15}\text{N}$ - NO$_3$ values in deep wells increased 1 month later. Labeled fertilizer accounted for as much as 0.74 milligram per liter of the nitrate in ground water.

INTRODUCTION

Water from about 20 percent of farmstead wells in Missouri contains concentrations of nitrate ($\text{NO}_3$) larger than the Missouri drinking-water standard of 10 mg/L as nitrogen [(N); Mesko and Garlson, 1988; Sievers and Fulhage, 1990; Ziegler and others, 1993a; Ziegler and others, 1993b]. Although N fertilizers are a suspected NO$_3$ source, other sources, such as animal waste and septic systems, have commonly been implicated. This study was designed to determine the input of NO$_3$ fertilizer to NO$_3$ concentrations in ground water. The nitrogen isotope composition ($\delta^{15}\text{N}$), in combination with ground-water chemistry and hydrologic monitoring, was used to investigate the movement of NO$_3$ through the hydrologic system from fertilizer applied to a field plot.

In order to perform a large number of $\delta^{15}\text{N}$ analyses for this study, a new technique for the collection and preparation of NO$_3$ from natural waters for determination of $\delta^{15}\text{N}$ - NO$_3$ (ratio of $^{15}\text{N}$ to $^{14}\text{N}$ in NO$_3$, relative to atmospheric N, expressed in per mil) analyses was developed in collaboration with the Stable Isotope Tracers Project of the National Research Program of the U.S. Geological Survey, Menlo Park, California. The technique combines the use of anion-exchange resins to concentrate NO$_3$ in the field and the Dumas combustion method (Fiedler and Proksch, 975) of preparation as modified by Kendall and Grim (1990). The combination of these methods facilitates the collection, concentration, storage, and shipment of NO$_3$ samples, and decreases the time and expense involved in laboratory preparation.
The purpose of this paper is to present preliminary results of a study of nitrogen isotope-tracer movement beneath a field plot and a test of the sample-preparation technique.

USE OF ANION EXCHANGE RESINS FOR NITROGEN ISOPOTE ANALYSIS

Field activities for the resin technique involved the concentration of dissolved NO$_3$ onto anion-exchange resins. Filtered-sample solutions were dripped through resin-filled columns at a uniform flow rate. Sample solutions were analyzed to confirm that more than 99 percent of NO$_3$ was removed from the sample.

The NO$_3$ can be removed from the resins with an eluant that either contains anions with a stronger affinity for the resin or a much higher concentration of an ion with lower affinity. After some experimentation, hydrochloric acid (HCl) was chosen as the eluant (table 1). This allowed for the concentration of NO$_3$ [initially in a 250 to 1,000 mL sample] into 15 mL of desorbate. Nitrate analyses of the desorbate indicated that at least 95 percent of the NO$_3$ was removed from the resins and preliminary isotope data indicated that nearly 100 percent of the NO$_3$ was recovered from the resins. Initial experiments, using a solution of known $\delta^{15}$N - NO$_3$, indicate that a precision of about 0.05 per mil is possible. Also, the concentrated desorbate facilitates sample storage, shipment, and preparation for the mass spectrometer by decreasing sample volume. It also eliminates the need for mercuric chloride (HgCl$_2$) or sulfuric acid (H$_2$SO$_4$) preservatives.

The possible effects of interfering anions commonly present in natural waters are being investigated. Sample solutions of a potassium nitrate (KNO$_3$) standard with a known $\delta^{15}$N - NO$_3$ were prepared. These standards were spiked with differing concentrations of

<table>
<thead>
<tr>
<th>Elutant solution</th>
<th>Percent recovery of nitrate in desorbate</th>
<th>Associated problems</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saturated potassium citrate</td>
<td>&lt;25</td>
<td>Poor recovery of nitrate; reaction with Vycor glass tubes causes combustion tube failure</td>
</tr>
<tr>
<td>Saturated calcium citrate</td>
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<td>Poor recovery of nitrate</td>
</tr>
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</tr>
<tr>
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<td>&gt;95</td>
<td>Hydrous CaCl$_2$ salt cumbersome to handle and dry</td>
</tr>
<tr>
<td>2.6 M SrCl$_2$</td>
<td>&gt;95</td>
<td>Hydrous SrCl$_2$ salt cumbersome to handle and dry</td>
</tr>
<tr>
<td>4.0 M KCl</td>
<td>&gt;95</td>
<td>Reaction with Vycor glass causes combustion tube failure</td>
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<tr>
<td>0.4 M H$_2$SO$_4$</td>
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</tr>
<tr>
<td>1.0 M HCl</td>
<td>50-80</td>
<td>Poor recovery of nitrate</td>
</tr>
<tr>
<td>3.0 M HCl</td>
<td>&gt;95</td>
<td>Sample must be neutralized before drying</td>
</tr>
</tbody>
</table>
chloride (Cl) and dissolved organic carbon (DOC). Initial results indicated large concentrations of Cl and DOC can prevent some of the NO\textsubscript{3} from being adsorbed, but not at concentrations detected in water sampled at the field study site.

Final laboratory preparation for isotopic analysis involved neutralizing and freeze-drying the desorbate, and combusting the dried salt by the Dumas technique (Fiedler and Proksch, 1975). As modified by Kendall and Grim (1990), the Dumas technique dissociates NO\textsubscript{3} salts at high temperature in a closed tube in the presence of copper (Cu), copper oxide (CuO), and calcium oxide (CaO). The Cu and CuO convert various N species to nitrogen gas (N\textsubscript{2}), while the CaO reacts with residual water (H\textsubscript{2}O) and carbon dioxide (CO\textsubscript{2}). The combustion method, in comparison to the traditional method outlined by Bremner (1965) and Bremner and Edwards (1965), is much faster (thereby decreasing laboratory costs) and eliminates many possible sources of contamination and isotopic fractionation.

**MOVEMENT OF 15 N AT THE FIELD PLOT**

A tracer plot was installed at the Missouri Management Systems Evaluation Area near Centralia, Missouri (fig. 1). The plot covers 0.1 acre and has 17 in. of silty loam topsoil overlying about 24 in. of low-permeability claypan. The claypan is underlain by about 55 ft of loess and glacial till that comprise the surficial aquifer.

Plot instrumentation includes a rainfall collector, a continuous-recording flume, an automatic runoff sampler, interflow collectors, 2 neutron-probe access tubes, 8 gravity lysimeters, 8 suction lysimeters, 14 monitoring wells, and 6 tensiometers (fig. 1). The plot is bordered by a 6-in.-high berm and a subsurface-water barrier to prevent offsite runoff and soil water from moving onto the plot. Conventional tillage was used on corn during 1991 and 1992, and fertilizer was applied at a rate of 83 lbs per acre in 1991. Background concentrations of various N species and 15 N - NO\textsubscript{3} were determined from May 28, 1991, through May 12, 1992. The dominant species of N in soil and ground water was NO\textsubscript{3}, however, organic N concentrations were substantial in runoff. On May 13, 1992, 3,800 g of NO\textsubscript{3} fertilizer with a δ\textsuperscript{15}N value of 3,080 per mil (spiked fertilizer) was applied as a liquid and tilled into the top 4 in. of soil just before planting. This enrichment was chosen so that even small contributions of spiked fertilizer could be detected in surface and ground water but low enough to prevent analytical problems. The cost of the enriched fertilizer was $6,000.

A hydrologic budget was calculated for the plot from May 28, 1991, through May 15, 1992 (Kelly and Blevins, 1993). About 53 percent of the 30.3 in. of rainfall was lost to evapotranspiration, 36 percent recharged ground water, 10 percent was lost to runoff, and 1 percent was lost as interflow. The δ\textsuperscript{15}N - NO\textsubscript{3} values in three samples of rainfall were 0.2, 0.5, and 1.2 per mil. Data from the National Atmospheric Deposition Program (1992) collected at a site about 50 mi south of the plot indicate that annual loadings of N in rainfall on the plot average about 180 g per year or about 4.8 percent of the N applied as fertilizer.

The δ\textsuperscript{15}N - NO\textsubscript{3} values in two prespike storms were 11.4 and 12.2 per mil (table 2). Background total 15 N in four topsoil samples ranged from 7.7 to 9.1 per mil and averaged 8.5 per mil. Therefore, the background δ\textsuperscript{15}N in runoff was about 10 per mil. The first runoff event following spike application had one of the larger NO\textsubscript{3} concentrations (2.1 mg/L) and the largest 15 N enrichment from the spike. The δ\textsuperscript{15}N - NO\textsubscript{3} value in the runoff sample was 1,065 per mil, and the spike was applied as NO\textsubscript{3}. Therefore, 34 percent of the NO\textsubscript{3} in the storm-composited runoff sample was from the recently applied spiked fertilizer. Nitrogen in harvested grain accounted for 22.2 percent of the spiked fertilizer, leaving 65.1 lbs per acre of the spiked N available for leaching, runoff, and denitrification.

Denitrification in clay-rich soils and aquifers can cause a significant loss of N. However, analyses of soil-gas samples collected after application of the spiked N fertilizer indicate that no significant denitrification occurred. The N\textsubscript{2} to argon (Ar) ratios were nearly identical to those in the atmosphere and δ\textsuperscript{15}N values of soil gas were nearly identical to those in the atmosphere (table 3). Also, concentrations of dissolved oxygen in ground water ranged from 1.9 to 10.1 mg/L. Near zero concentrations of dissolved oxygen are expected if denitrification is substantial. Therefore, denitrification is not present in the saturated zone.

The spiked fertilizer was detected in the shallowest suction lysimeters (1.5 ft deep) on June 1 (125 per mil); however, it was not detected in soil moisture at depths of 3.0 and 4.0 ft during the growing season (from May through October). Values of δ\textsuperscript{15}N - NO\textsubscript{3} in suction lysimeter samples collected in November and December ranged from 516 to 835 per mil.
Figure 1. Instrumentation at study plot.
Table 2. Analyses of $\delta^{15}$N in samples collected at the field plot near Centralia, Missouri

[--; no data]

<table>
<thead>
<tr>
<th>Source (fig. 1)</th>
<th>Well depth (in feet)</th>
<th>Date collected</th>
<th>$\delta^{15}$N (total nitrogen, per mil)</th>
<th>$\delta^{15}$N - NO$_3$ (dissolved nitrate, per mil)</th>
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<tbody>
<tr>
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</table>
Table 2. Analyses of $\delta^{15}N$ in samples collected at the field plot near Centralia, Missouri—"Continued"

<table>
<thead>
<tr>
<th>Source (fig. 1)</th>
<th>Date collected</th>
<th>$\delta^{15}N$ (total nitrogen, per mil)</th>
<th>$\delta^{15}N$ - NO$_3$ (dissolved nitrate, per mil)</th>
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</thead>
<tbody>
<tr>
<td>Storm runoff</td>
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<tr>
<td>(storm-composite samples)</td>
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</tr>
<tr>
<td>Topsoil at E0</td>
<td>1-06-92</td>
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</tr>
<tr>
<td>Topsoil at W0</td>
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<tr>
<td>Grain</td>
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</tr>
<tr>
<td>Grain</td>
<td>10-14-92</td>
<td>648</td>
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<tr>
<td>Stover$^1$</td>
<td>10-14-92</td>
<td>670</td>
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$^1$The part of corn above the ground, except for grain.

Table 3. Soil-gas analyses

[-- no data]

<table>
<thead>
<tr>
<th>Depth of sample collection (in feet)</th>
<th>Molar nitrogen to argon ratio</th>
<th>$\delta^{15}N$ relative to atmospheric nitrogen</th>
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<td></td>
<td>6-24-92</td>
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</tr>
<tr>
<td>4.0</td>
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<td>--</td>
</tr>
<tr>
<td>atmospheric gas</td>
<td>83.6</td>
<td>83.6</td>
</tr>
</tbody>
</table>

406
The gravity lysimeters, constructed to intercept ground-water recharge, did not yield water between the application of spiked fertilizer and November 12, 1992. The $\delta^{15}$N - NO$_3$ in the first gravity-lysimeter samples collected in November had enrichment that ranged from 297 to 1,145 per mil. Values of $\delta^{15}$N - NO$_3$ in gravity lysimeter samples collected from December 1, 1992, through January 4, 1993, ranged from 665 to 1,050 per mil; that is, about 30 percent of the NO$_3$ in gravity lysimeter samples came from the spiked N fertilizer.

Background $\delta^{15}$N - NO$_3$ in 15 ground-water samples collected from 8 wells from June 27, 1991, through May 12, 1992, ranged from 9.9 to 15.5 per mil, with an average of 11.8 per mil. Background concentrations of NO$_3$ ranged from 4.0 to 45.5 mg/L, averaged 20.8 mg/L, and accounted for more than 95 percent by weight of all dissolved N in ground water. The spike was applied in May 1992 and no spiked fertilizer was detected in ground water by August 10-11. The constant decline of water levels indicates minimal recharge during this time (fig. 2). This minimal recharge is caused by the large quantity of evapotranspiration that typically occurs in agricultural crops within this region. In fact, spiked fertilizer probably did not reach ground water until substantial ground-water recharge from fall rain began after November 12 (fig. 2). About 0.24 mg/L of spiked fertilizer was detected in the two shallowest wells, W0 and E0, as soon as 6 days after the rain began. Twenty-eight days later, after continued recharge, spiked N fertilizer in well E0 decreased slightly, but increased to 0.74 mg/L in well W0. Small quantities of spiked NO$_3$ were detected in samples from the intermediate depth wells E1 and M1 (table 2). However, the total contribution of N fertilizer to ground-water NO$_3$ cannot be determined for several years until the carry-over of NO$_3$ in the soil and glacial till from year to year can be determined.

**SUMMARY AND CONCLUSIONS**

A simplified procedure for $^{15}$N analysis of NO$_3$ in natural waters involves concentration of the NO$_3$ on anion exchange resins in the field and the modified Dumas combustion method. This procedure decreases laboratory preparation time and analysis cost. It also eliminates the need for toxic preservatives and decreases storage and shipment requirements. Precision of the method is currently about 0.05 per mil. High concentrations of dissolved CI and DOC can affect the accuracy of the method, but not at concentrations detected at the study site.

The N fertilizer applied to corn in the spring typically is not leached to ground water until after the fall rain, which occurs after the harvest. At this time, evapotranspiration is low and soils become saturated. About 22 percent of the N fertilizer applied was removed from the grain, leaving about 65 lbs per acre available for leaching, washoff, and denitrification. Soil-gas analyses and substantial quantities of dissolved oxygen in shallow ground water indicate denitrification was not a significant cause of loss of N in fertilizer.

Although small quantities of NO$_3$ reached ground water as soon as fall recharge occurred, the total contribution of N fertilizer to ground water cannot be determined until samples have been collected over several years to determine the carry-over of NO$_3$ in the soil and glacial till from one year to the next. One month after recharge began, less than 1 mg/L of the NO$_3$ in ground water was derived from spiked fertilizer. However, as of March 1993, enrichment of $\delta^{15}$N - NO$_3$ is still increasing in most wells.

With substantially decreased costs of $^{15}$N analysis, use of $^{15}$N may become feasible for many more field studies. However, the labeled fertilizer used in this study cost $6,000 for 0.1 acre and tracer studies over large areas are not likely unless substantial decreases in the cost of fertilizer enriched with $^{15}$N are achieved.
Figure 2. $\delta^{15}$N enrichment relative to atmospheric nitrogen, ground-water level in well E1, and precipitation—May 28, 1991, through December 31, 1992.
REFERENCES


Occurrence, Deposition, and Long Range Transport of Herbicides in Precipitation in the Midwestern and Northeastern United States

By Donald A. Goolsby, E. Michael Thurman, Michael L. Pomes, Michael Meyer, and William A. Battaglin

Abstract

Herbicides were detected in precipitation throughout the midwestern and northeastern United States during late spring and summer of 1990 and 1991. During May and June atrazine, alachlor, or both were detected in 60 to 75 percent of weekly accumulations of precipitation collected at 81 sampling sites in 23 States. Atrazine or alachlor were detected in at least one sample from all States, including samples from remote wilderness areas such as Isle Royale in northern Lake Superior. During the remainder of the year, herbicides generally were detected in weekly samples at less than about 20 percent of the sites. Atrazine was the most frequently detected herbicide, followed by alachlor, desethylatrazine, and metolachlor. Herbicide concentrations and frequency of detection were much higher in the Midwest than elsewhere. Precipitation-weighted herbicide concentrations for mid-April through mid-July typically were 0.2 to 0.4 µg/L (micrograms per liter) in the Midwest and weighted concentrations as large as 0.9 µg/L were present at a few sites. Concentrations of 1 to 3 µg/L were measured in a few individual samples representing small amounts of precipitation. Deposition rates for both atrazine and alachlor ranged from more than 200 (µg/m²)/yr (micrograms per square meter per year) at a few sites in the Midwest to less than 10 (µg/m²)/yr in the Northeast. These amounts represent less than 1 percent of the atrazine and alachlor applied annually to crops. The geographic pattern of herbicide deposition provides evidence for long-range atmospheric transport.

INTRODUCTION

Current agricultural practices in the United States require extensive use of herbicides for economical production of corn, soybeans, sorghum, and other row crops. Data compiled by Gianessi and Puffer (1991) show that about two-thirds of the 285 million kg of herbicides used annually in the United States (Aspelin and others, 1992) are used in crop production in the Midwestern United States, and principally in the Mississippi River drainage basin. As a consequence, the Midwest is the major source area for transport of herbicides into streams and ground water in the midcontinent as well as to the atmosphere. Most herbicides are relatively soluble but significant amounts (a few percent of the amounts applied) can be transported into streams (Baker and Richards, 1989; Goolsby and others, 1991; Thurman and others, 1992) and ground water (Hallberg, 1989; Holden and others, 1992; Kolpin and others, 1994). Previous research has also shown that herbicides and other organic compounds can be transported into the atmosphere by various processes. In the atmosphere, these compounds can be dispersed by air currents and redeposited on the land surface, lakes, and streams by rainfall, snow, and dry deposition, often at considerable distances from their origin. For example, the transport of chlorinated insecticides and

1U.S. Geological Survey, Lakewood, CO
2U.S. Geological Survey, Lawrence, KS
polychlorinated biphenyls (PCB’s) into the Great Lakes is believed to be largely from the atmospheric sources (Eisenreich and others, 1981). Herbicides have been reported in fog (Glotfelty and others, 1987) and rainfall in the midwestern United States (Capel and others, 1991; Nations and Hallberg, 1992; Richards and others, 1987; Williams and others 1992), eastern United States (Glotfelty and others, 1990; Wu, 1981), and in Europe (Buser, 1990; Trevisan, 1993). In spite of these studies, relatively little is known on a regional or multistate scale about deposition patterns of herbicides in precipitation and the magnitude of herbicide deposition in precipitation in comparison to quantities applied to cropland or to surface-runoff losses.

To learn more about herbicides in precipitation, a study was conducted during 1990 and 1991 to determine the occurrence and distribution of herbicides in precipitation (rain and snow) for a large part of the United States, including much of the Mississippi River basin where most of the herbicides are used. The study was conducted as part of the Toxic Substances Hydrology Program and was mass oriented in that it attempted to determine the mass deposited in precipitation over nearly one-quarter of the United States for the two most heavily used herbicides in the country, -- atrazine and alachlor (Gianessi and Puffer, 1991). Specific objectives of the study were to (1) determine the occurrence and temporal distribution of several major herbicides in precipitation, (2) estimate the amounts of atrazine and alachlor deposited in precipitation annually in individual States and over a large part of the conterminous United States, (3) relate annual deposition of atrazine and alachlor to amounts applied annually, and (4) compare annual herbicide deposition in precipitation within the Mississippi River basin to the estimated annual amount transported out of the basin in streamflow. A summary of results from this study is presented in this paper.

DESCRIPTION OF STUDY AREA AND DATA COLLECTION METHODS

The study area for this investigation encompassed 26 States (fig. 1). It includes States in the upper Midwest where the use of herbicides, such as atrazine and alachlor, is most intense, and States eastward to the Atlantic Ocean and northward to the Canadian border that potentially may receive atmospheric deposition of herbicides applied in the Midwest. Precipitation samples were obtained from the study area through the cooperation and assistance of the National Atmospheric Deposition Program / National Trends Network (NADP/NTN), Fort Collins, Colo., and the Illinois State Water Survey, Champaign, Ill. The National Atmospheric Deposition Program (1992) operates a network of about 200 sites nationwide to monitor the status and trends in acid deposition. Weekly accumulations of precipitation (rain and snow) were obtained at 81 NADP/NTN sampling sites located in 23 States within the 26-State study area (fig. 1). In addition, five NADP/NTN sites in high-elevation areas along the Rocky Mountains (fig. 1) and in Alaska (not shown on fig. 1) were sampled to provide background data on herbicides in precipitation at sites far from the study area. A complete description of each sampling site is given in a directory of precipitation monitoring sites (National Atmospheric Deposition Program, 1986). Collection of samples began in March 1990 and continued through September 1991—a period of 19 months.

Each NADP/NTN monitoring site is equipped with an Aerochem Metrics Wet/Dry collector to collect precipitation and a separate Belfort 5-780 Universal Rain Gage to make an independent measurement of precipitation amount. The wet/dry collectors are equipped with two 13-liter polyethylene buckets that alternately collect wet or dry deposition. The “wet side” bucket is covered with a tight fitting lid until precipitation begins, at which time a heated sensor opens the lid to allow collection of wet deposition. When precipitation ceases, the sensor closes the lid until the next precipitation event. Precipitation is accumulated in this manner for a period of 1 week. Each Tuesday, regardless of whether precipitation has occurred the previous week, a site operator removes the “wet side” bucket, seals it with a polyethylene lid, and sends it to the Central Analytical Laboratory (CAL) operated by the Illinois State Water Survey in Champaign, Ill. for analysis. For the 86 NADP/NTN sites used in this study, a subsample was obtained from the polyethylene buckets upon receipt at the CAL. The subsample, consisting of 10 to 125 mL (milliliters), depending on the amount of precipitation collected, was transferred to a 125-mL baked glass bottle, chilled, and sent to the U.S. Geological Survey’s laboratory in Lawrence, Kans., for herbicide analysis. Buckets from sites where no precipitation occurred were leached for 24 hours with 50 mL of distilled water, which then was used as a system blank. Subsamples of these blanks were provided by the CAL for herbicide analysis. Only
herbicides deposited in precipitation (rain and snow) were analyzed in this study. No samples of dry deposition were analyzed.

All precipitation samples were analyzed by enzyme-linked immunosorbent assay (ELISA) for both alachlor and atrazine. The reporting limits for ELISA were 0.1 µg/L for atrazine and 0.2 µg/L for alachlor. Samples in which herbicides were detected and that had a sample volume of at least 60 mL were confirmed by gas chromatography/mass spectrometry (GC/MS). Analysis of samples with less than 60 mL were not confirmed. About 10 percent of all samples that were found to contain no herbicides by ELISA also were analyzed by GC/MS. These samples were chosen randomly from all negative samples. An exception to the above procedure occurred during the first few months of the study when 20 percent of all samples with 60 mL or more of water were randomly selected for GC/MS analysis regardless of whether herbicides were detected by ELISA. Of about 6,000 samples analyzed by ELISA during the study, more than 2,200 were confirmed by GC/MS analysis. Included in the 6,000 samples were about 1,200 samples analyzed by ELISA and 400 samples analyzed by GC/MS that were used for quality-assurance (QA) purposes.

Samples for ELISA analysis were analyzed in duplicate (Pomes and others, 1991) using microtiter plates. Concentrations were determined with a microtiter plate reader and calibration curves were developed from four standard solutions of known atrazine or alachlor concentration that ranged from 0 to 5 µg/L. Samples were analyzed in duplicate and the results averaged. Standards were analyzed in triplicate.
or quadruplicate. GC/MS samples were analyzed by an automated procedure (Thurman and others, 1990) following solid-phase extraction of samples on C18 cartridges. Samples were analyzed for 11 parent herbicides: alachlor, ametryn, atrazine, cyanazine, metolachlor, metribuzin, prometon, prometryn, propazine, simazine, and terbutryn, and two metabolites of atrazine—desethylatrazine and desisopropylatrazine. Several experiments conducted on the NADP/NTN plastic collection buckets over periods of 3 weeks confirmed that no significant sorption, degradation, or other losses of the major herbicides studied occurred in the buckets. However, the buckets contributed a compound with a GC/MS peak that interfered with the identification of desisopropylatrazine in some of the samples.

Linear-regression equations, given below, were developed from more than 2,200 samples analyzed for atrazine and alachlor by both ELISA and GC/MS. Because of slight changes in methodology and differing batches of ELISA kits, regression results were improved by developing separate equations for samples collected in 1990 and 1991.

- 1990: atrazine = -0.01 + 0.70 ELISA. $R^2 = 0.94$; standard error of estimate = 0.09 µg/L.
- 1991: atrazine = 0.00 + 0.80 ELISA. $R^2 = 0.78$; standard error of estimate = 0.10 µg/L.
- 1990: alachlor = 0.00 + 0.64 ELISA. $R^2 = 0.76$; standard error of estimate = 0.08 µg/L.
- 1991: alachlor = 0.00 + 0.84 ELISA. $R^2 = 0.86$; standard error of estimate = 0.09 µg/L.

These equations were used to estimate concentrations of atrazine and alachlor in about 3,700 samples (including quality assurance samples) analyzed only by ELISA. The measured or estimated concentrations and precipitation amounts were then used to calculate weekly deposition of these two herbicides at each sampling site which were expressed as micrograms per square meter ($\mu g/m^2$) per week.

RESULTS AND DISCUSSION

Ten of the 13 herbicides and metabolites analyzed in this study were detected in precipitation samples from the 81 sampling sites in the study area (table 1). Atrazine and alachlor were detected (at concentrations of 0.1 to 0.2 µg/L or greater) by ELISA in 26.2 percent and 9.0 percent of the samples, respectively. These two herbicides were detected (at concentrations of 0.05 µg/L or greater) in 33.9 and 21.5 percent, respectively, of the samples selected for analysis by GC/MS. However, it should be stated that this is a biased result since the samples for GC/MS analysis were previously screened by ELISA for the presence or absence of herbicides. Consequently these results are not typical of the frequency of occurrence of these herbicides in the 6,000 samples collected during the period of this study. Desethylatrazine was the third most frequently detected compound in the ELISA-screened samples (19.5 percent), followed by metolachlor (14.9 percent), and cyanazine (8.1 percent). Five other herbicides and metabolites (table 1) were detected in 3 percent or fewer of the samples. Only about 1 percent of the samples had herbicide concentrations exceeding 1 µg/L. Because of the proximity of some sampling sites to cropland, spray drift cannot be ruled out as a possible source for some of the high concentrations. Atrazine and alachlor were detected in concentrations near the analytical reporting limit (see table 1) in a small number of samples from sites located in the background area (fig. 1.).

The spatial pattern of occurrence and temporal distribution of atrazine and alachlor in precipitation is similar to the pattern observed in streams throughout the Midwest (Goolsby and others, 1991; Thurman and others, 1992). The frequency at which these two herbicides were detected each week at sampling sites throughout the study area (fig. 1) began to increase in mid-April following application of herbicides to cropland, and peaked in mid-June or early July (fig. 2). During this period, atrazine was detected each week at 60 to 75 percent of the sites sampled and alachlor was detected at 30 to 40 percent of the sites. During the remainder of the year, these herbicides generally were detected at less than about 20 percent of the sites sampled. Samples were not collected at all sites each week because of periods of no precipitation (fig. 2). Atrazine and alachlor were detected most frequently at sites in the Midwest, but at least one sample (confirmed by GC/MS) from all 23 States with sampling sites had detectable concentrations of one or both herbicides. These sites included sites in areas remote from cropland such as Maine and Isle Royale in northern Lake Superior. The processes by which these and other herbicides are transported into the atmosphere include volatilization (primarily from moist soils), attachment to soil and dust particles that are blown into the atmosphere, and spray drift during application. Of these processes, volatilization is believed to be predominant (Tierney, 1993). Atrazine is about 10 times less volatile than alachlor and has a longer soil half-life (about 60 days) than alachlor (about 15 days). Consequently, it volatilizes into the atmosphere at a slower rate and is available for volatilization from the soil for a longer period of time than is alachlor. Because of these properties, atrazine is present in precipitation for a longer time than is alachlor (fig. 2).
Table 1. Statistical summary of herbicide concentrations measured in precipitation samples from 81 National Atmospheric Deposition Program/National Trends Network sites during March 1990 through September 1991

<table>
<thead>
<tr>
<th>Herbicide</th>
<th>Reporting limit µg/L</th>
<th>Number of samples</th>
<th>Percent detections</th>
<th>Concentration, in µg/L, for indicated percentiles</th>
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<tr>
<td></td>
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</tr>
<tr>
<td>ELISA¹ Analysis (all samples)</td>
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<tr>
<td>atrazine</td>
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<td>0.2</td>
<td>4,764</td>
<td>9.0</td>
<td>&lt;2</td>
</tr>
<tr>
<td>GC/MS² Analysis (samples pre-screened by ELISA)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>atrazine</td>
<td>0.05</td>
<td>1,848</td>
<td>33.9</td>
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</tr>
<tr>
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<td>1,849</td>
<td>21.5</td>
<td>&lt;0.05</td>
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<tr>
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<td>19.5</td>
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<tr>
<td>metolachlor</td>
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<td>14.9</td>
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</tr>
<tr>
<td>cyanazine</td>
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<td>8.1</td>
<td>&lt;0.05</td>
</tr>
<tr>
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<td>1,849</td>
<td>3.0</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>simazine</td>
<td>0.05</td>
<td>1,849</td>
<td>1.6</td>
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</tr>
<tr>
<td>metribuzin</td>
<td>0.05</td>
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<td>0.7</td>
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<tr>
<td>prometon</td>
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<td>0.5</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>propazine</td>
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<td>1,849</td>
<td>0.1</td>
<td>&lt;0.05</td>
</tr>
</tbody>
</table>

¹ELISA, enzyme-linked immunosorbent assay
²GC/MS, gas chromatography/mass spectrometry.

Figure 2. Frequency of atrazine and alachlor detections, by week, for 81 sites in study area (midwestern and northeastern United States). Includes detections by immunoassay and gas chromatography/mass spectrometry. Immunoassay reporting limits are 0.1 and 0.2 micrograms per liter respectively for atrazine and alachlor and 0.05 micrograms per liter for gas chromatography-mass spectrometry.

Atrazine and alachlor concentrations were highest and detections were most frequent at sites in the Midwest (fig. 3) where these herbicides are used most extensively. Concentrations as high as 3 µg/L were detected in individual samples at some sites. In areas where the use of atrazine and alachlor are similar such as Iowa, Illinois, and Indiana, alachlor concentrations generally were higher than atrazine concentrations (fig. 3), in part, because of the greater volatility of alachlor relative to that of atrazine. In remote areas such as Maine and parts of Michigan, herbicide concentrations were very low and detections were infrequent (fig. 3). The highest herbicide concentrations tended to occur during small
Figure 3. Atrazine and alachlor concentrations in precipitation, and precipitation amounts. March 1990 through September 1991. Some herbicide concentrations estimated from immunoassay-gas chromatography/mass spectrometry regression equations.
precipitation events after herbicide application, because the first part of a precipitation event flushes most of the herbicides from the atmosphere (Capel, 1991). Subsequent precipitation dilutes the concentrations from the earlier precipitation. Therefore, it is difficult to make meaningful comparisons of herbicide concentrations among sites or over time on the basis of individual weekly samples. A better comparison can be made with precipitation-weighted concentrations, which are calculated by summing the product of precipitation amounts and herbicide concentrations over a period of time, such as 3 months, and dividing by the total amount of precipitation. Precipitation-weighted concentrations of atrazine and alachlor calculated for a 13-week period from mid-April through mid-July 1991 are shown in figure 4; the map was constructed using a geographic information system (GIS). Precipitation-weighted concentrations of 0.2 to 0.4 µg/L are typical throughout the Midwest and weighted concentrations of 0.4 to 0.9 µg/L were detected at sites in Iowa, Illinois, and Indiana. The spatial pattern of weighted concentrations reflects the intensity of use of these two herbicides. It also provides tentative evidence for long-range atmospheric transport of herbicides.

The estimated masses of atrazine and alachlor deposited in precipitation during January through September 1991 are shown in figure 5. The deposition rates range from more than 200 µg/m² for both herbicides at a few sites in the Midwest to less than 10 µg/m² in the Northeast. Most of the deposition occurs during April through July. The deposition patterns are somewhat similar for the two herbicides, except in the western part of the study area (Nebraska and Kansas) where alachlor deposition is considerably less than atrazine deposition, reflecting the different usage patterns of these herbicides. The total mass of herbicides deposited in precipitation over the entire study area during 1991 is estimated to be 140,000 kg for atrazine and 82,000 kg for alachlor. These amounts represent about 0.6 and 0.4 percent of the atrazine and alachlor applied to cropland in the study area. These percentages are smaller than volatilization losses reported in the literature (Taylor and Glotfelty, 1988). There are many possible reasons for the relatively small measured amounts including dry deposition of herbicides between precipitation events, photochemical degradation of herbicides in the atmosphere, especially atrazine (Gates and others, 1991; Pelizzetti and others, 1990), atmospheric transport of herbicides beyond the study area, and inadequate analytical detection limits, especially for the ELISA methods.

The amount of atrazine deposited annually in precipitation appears to be somewhat smaller than the amount transported to streams in surface runoff, whereas the annual deposition of alachlor appears to be somewhat larger than the amount transported in surface runoff. For example, in a recent study (Battaglin and others, 1993) estimated that 321,000 kg of atrazine and 33,700 kg of alachlor were discharged from the Mississippi River basin to the Gulf of Mexico in streamflow during a 1-year period, while the amounts of these herbicides used in the basin were approximately equal. In comparison, it is estimated from this study that about 110,000 kg of atrazine and 68,000 kg of alachlor are deposited annually on the Mississippi River basin in precipitation. These quantities could be considerably larger if the amounts of dryfall were known. These results indicate that more alachlor is deposited through precipitation in the Mississippi River basin than is transported out of the basin in streamflow, whereas the opposite relation could be true for atrazine.

**SUMMARY**

Results from this study indicate that significant amounts of atrazine and alachlor are lost through volatilization and that these losses can be comparable to losses transported in surface runoff. Because of its comparatively higher volatility and shorter soil half-life, considerably more alachlor appears to volatilize than is transported by surface-runoff losses. Additional unmeasured amounts of herbicides were likely present in dry deposition. Further research is needed to determine the relative amounts of herbicides, insecticides, and other organic compounds, including photochemical degradation products, deposited in wet and dry deposition. Several other extensively used herbicides such as 2,4-D, EPTC, and trifluralin are considerably more volatile than atrazine and alachlor and might be present in atmospheric deposition in substantial amounts.
Figure 4. Precipitation-weighted concentrations of atrazine and alachlor throughout the midwestern and northeastern United States, April 16 through July 16, 1991.
Figure 5. Estimated deposition of atrazine and alachlor in precipitation throughout the midwestern and northeastern United States, January through September 1991.
REFERENCES


Atrazine Transport and Degradation in a Pristine Watershed: The Fate of Atrazine Deposited by Precipitation

By Aron E. Cromwell and E. Michael Thurman

Abstract

Atrazine used in agricultural areas is being transported atmospherically and deposited by precipitation onto pristine watersheds. The fate of atrazine was studied at Isle Royale National Park, an island park located in Lake Superior on the United States-Canadian border. Samples of rainfall, soil water, surface water, and soils were analyzed by combining solid-phase extraction (SPE) with enzyme-linked immunosorbent assay (ELISA). This SPE-ELISA combination enabled the field analysis of water samples in which the concentrations of atrazine were as small as 5 ng/L (nanograms per liter). The SPE-ELISA results were confirmed using gas chromatography/mass spectrometry (GC/MS) with isotope dilution. Maximum atrazine concentrations in rainfall occurred in late spring, approaching the U.S. Environmental Protection Agency Maximum Contaminant Level (MCL) for drinking water of 3.0 micrograms per liter. By mid-summer, rainfall concentrations of atrazine had decreased to less than 5 ng/L. Atrazine was found in small concentrations in water from all lakes that were sampled. Field data indicate that atrazine degrades rapidly in soil environments but more slowly in aquatic environments. This slow degradation rate in water has important implications for the quality of lakes in pristine areas receiving atrazine-contaminated rainfall because of the potential for accumulation of atrazine in the ecosystem.

INTRODUCTION

Since World War II, American farmers have greatly improved crop yields by using increased amounts of chemically manufactured herbicides. The most frequently used herbicide in the Midwest is a triazine called atrazine (6-chloro-N-ethyl-N’-(1-methylethyl)-1,3,5-triazine-2,4-diamine; 2-chloro-4-ethylamino-6-isoproplyamine-s-triazine) (Goolsby, Thurman, and Kolpin, 1990). Atrazine generally is applied as a preemergent herbicide to control broadleaf weeds in corn (Zea mays L.) and grain sorghum [Sorghum bicolor (L.) Moench].

Due to concern for water quality, the amount and fate of atrazine transported by agricultural runoff to waters of the Corn Belt have been studied to great lengths (Humenik and others, 1987; Thurman and others, 1992). Additionally, it has been discovered that significant amounts of atrazine can be transported atmospherically (Glotfelty and others, 1983; Richards and others, 1987). This finding indicates that atrazine could be transported atmospherically from agricultural areas and then deposited by precipitation onto pristine areas.

The concentration of atrazine in precipitation can be determined accurately and inexpensively by using a method of environmental analysis called enzyme-linked immunosorbent assay (immunoassay, or ELISA) (Bushway and others, 1988; Goolsby Thurman, Clark, and Pomes, 1990; Thurman and others, 1990). When ELISA is coupled to a concentration process like solid-phase extraction (SPE), the detection level is lowered (D. S. Aga and E. M. Thurman, U.S. Geological Survey, written commun., 1993).

This lower detection level facilitates the study of the fate of atrazine transported atmospherically into a pristine environment. Precipitation, lake-water, and soil-water samples were collected and analyzed in a pristine watershed in order to determine the occurrence
and fate of atrazine deposited by precipitation. The fate of atrazine is of great importance because it will affect aquatic plant and animal communities if concentrations accumulate to sufficiently high levels (deNoyelles and others, 1982; Jones and Winchell, 1984).

DESCRIPTON OF STUDY AREA AND SAMPLE COLLECTION

The study area was Isle Royale National Park, Michigan. The 550-km² (square kilometer) island is located in Lake Superior on the United States-Canadian border. The park is protected from excessive human influence by its Congressional designation as a Wilderness Area and its United Nations designation as an International Biosphere Reserve. Isle Royale has never had any history of herbicide application and, being an island, is isolated from inflow from herbicide-contaminated areas. These facts suggest that all of the atrazine found in the hydrologic system of Isle Royale would be from precipitation. Also, Isle Royale is located approximately 1,000 km (kilometers) northeast of the Corn Belt. The northeast relation of the island to the Corn Belt places the island directly in the path of spring storms carrying the triazines.

A previous study by D. A. Goolsby (U. S. Geological Survey, written commun., 1993) identified atrazine in rain samples from Isle Royale. In order to confirm this finding and to determine the fate of atrazine in a pristine watershed, two data-collection sites were established at Isle Royale. The sites were located near two lakes on Isle Royale, Lake Richie and Wallace Lake (fig. 1). Rainfall, soil water, and surface water were collected from the two sites from mid-May through mid-July 1992.

Bulk precipitation was collected using low-density polypropylene funnels connected to 4-L (liter) baked amber-glass bottles. After each rain, bulk precipitation was transferred from the collectors to 125-mL (milliliter) baked amber-glass bottles. The collectors then were washed in soap and deionized water and rinsed in deionized water before reuse. Three of these collectors were placed at each of the two field sites. Approximately 100 rainfall samples were collected during the 1992 season.

Soil water was collected in suction-cup lysimeters. The polyvinyl-chloride lysimeters had porous porcelain cups at their base. Twelve lysimeters were installed near Wallace Lake, and six lysimeters were located near Lake Richie. At both sites lysimeters were paired, one 15-centimeter (cm) with one 30-cm depth lysimeter. After each rain, a hand pump was used to apply a vacuum to the lysimeters. The following day, the water in the lysimeters was pumped into 125-mL baked amber-glass bottles. Precleaned Teflon tubing was used for the transfer.

Surface water was collected and analyzed in order to determine the extent of herbicide contamination in the watershed. During the herbicide deposition season (from May to July) a total of 20 depth-integrated samples were collected from Wallace Lake and Lake Richie. In August of 1992, surface-water samples were collected from lakes across Isle Royale. This survey entailed the sampling of 12 major lakes on Isle Royale (fig. 1) including Wallace Lake and Lake Richie, which were also sampled earlier in the season. Samples were collected in 125-mL and 1,000-mL baked amber-glass bottles. Results from the August 1992 lake sampling are located in Table 1.

METHODS

Reagents

Methanol and ethyl acetate were the pesticide-grade solvents used. The SPE cartridges that were used contained 360-mg (milligrams) of 40-μm (micrometer) C₁₈-bonded silica. Standard stock solutions were prepared in methanol, and phenanthrene-d₁₀ was used as an internal standard for GC/MS analysis.

Solid-Phase Extraction

The SPE procedure was performed manually at Isle Royale but was automated when performed in the laboratory. The manual method used a vacuum manifold to pass liquids through the C₁₈ cartridges. The automated method used a computerized robotic workstation to process the samples. In both methods, the cartridges were washed sequentially with 2 mL methanol, 6 mL ethyl acetate, 2 mL methanol, and 2 mL distilled water. One hundred (100) mL of sample were passed through the prewashed cartridge for the automated method, while 123 mL of sample were used in the manual procedure. The sample passed through the cartridge at a flow rate of 10 mL/min (milliliters per minute) or slower. The cartridge then was eluted with 3 mL ethyl acetate followed by a transfer step to
Figure 1. Location of study area.
remove the ethyl acetate (top layer) from the residual water (bottom layer) in the eluate. The ethyl acetate then was evaporated to dryness using a hot-water bath and a stream of air when processed at Isle Royale or using a stream of nitrogen when processed in the laboratory. The dried sample was reconstituted with 1 mL of 20/80 (% v/v) methanol/water for analysis by ELISA (D. S. Aga and E. M. Thurman, U.S. Geological Survey, written commun., 1993).

Gas Chromatography/Mass Spectrometry

GC/MS analysis of the eluates was performed on a mass selective detector (MSD). Operating conditions were identical to those described by Thurman and others (1990).

RESULTS AND DISCUSSION

Enzyme-Linked Immunosorbent Assay

The ELISA analysis was performed with assay kits using polyclonal antibodies coated on paramagnetic beads. The samples were analyzed according to the directions supplied with the kits. The optical densities were read using the photometric analyzer, and the analyte concentrations were calculated on the basis of a linear regression of linear/logit-transformed data. The calibration standards for atrazine were prepared at concentrations of 5.0, 1.0, 0.10, and 0 μg/L (micrograms per liter) using 20/80 (% v/v) methanol/water solvent, the same solvent used to reconstitute the analyte.

Atrazine in Rainfall

Atrazine was detected at significant levels (above 50 ng/L) in the rainfall samples collected from Isle Royale between mid-May and late-June 1992. Atrazine concentrations in rainfall samples collected during 1992 are shown in figure 2. Also represented in figure 2 is the concentration of atrazine in the rainfall sample multiplied by the amount of rainfall associated with that rain sample (in millimeters). This calculated number is related to the mass of atrazine associated with a particular rain. The maximum atrazine concentration measured in rainfall occurred on June 3 at about 1.9 μg/L, and the maximum atrazine

Table 1. Concentrations of atrazine on surface-water samples from Isle Royale National Park, Michigan, August 1992

<table>
<thead>
<tr>
<th>Data collection sites (fig. 1)</th>
<th>Average concentration (nanograms per liter)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chippewa Harbor</td>
<td>6.6</td>
</tr>
<tr>
<td>Lake Whittlesey</td>
<td>3.6</td>
</tr>
<tr>
<td>Wood Lake</td>
<td>10.1</td>
</tr>
<tr>
<td>Siskiwit Lake (9 sites)</td>
<td>10.6</td>
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<tr>
<td>Lake Desor (4 sites)</td>
<td>13.2</td>
</tr>
<tr>
<td>Intermediate lake (2 sites)</td>
<td>10.3</td>
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<td>Lake Richie (4 sites)</td>
<td>6.6</td>
</tr>
<tr>
<td>Lake LeSage (2 sites)</td>
<td>9.0</td>
</tr>
<tr>
<td>Lake Livermore</td>
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</tr>
<tr>
<td>Lake Chickenbone</td>
<td>6.5</td>
</tr>
<tr>
<td>Wallace Lake</td>
<td>6.9</td>
</tr>
<tr>
<td>Lake Feldtmann surface (6 sites)</td>
<td>11.8</td>
</tr>
<tr>
<td>Lake Feldtmann depth 1.0 feet (6 sites)</td>
<td>11.7</td>
</tr>
</tbody>
</table>
mass was measured on June 6. These values were much larger than anticipated, so GC/MS analysis was performed on these samples for confirmation. The GC/MS results agreed with the ELISA results. Additionally, the GC/MS analysis enabled the testing for additional herbicides and metabolites. These results identified the presence of the herbicide cyanazine as well as two triazine metabolites, deethylatrazine and deisopropylatrazine. On June 3, concentrations of cyanazine in rainfall approached the U.S. Environmental Protection Agency Health Advisory Level of 1.0 µg/L for drinking water (U.S. Environmental Protection Agency, 1992). Furthermore, on June 3 and June 6, GC/MS analysis revealed the presence of the triazine metabolites deethylatrazine and deisopropylatrazine at concentrations between 0.10 and 0.20 µg/L. After June 6, the concentration of atrazine in the rainfall decreased, and by mid-July no appreciable mass of atrazine was present.

Atrazine Degradation and Transport in Soil The concentration of atrazine in soil water in one lysimeter near Wallace Lake is shown in figure 3. Because soil types and rates of transport can differ from one lysimeter to the next it was not appropriate to combine the data from different lysimeters. Samples from most lysimeters followed the general concentration trend of the lysimeter depicted in figure 3, which is similar to the shape of the curve that depicts mass shown in figure 2 for rainfall samples. The small concentrations of atrazine in the soil water indicate that degradation of the herbicide takes place rapidly in the soil medium. Although concentrations of atrazine in soil water are considerably smaller than the concentrations in the rainfall, the degradation process is not complete.

Figure 2. Concentration and mass of atrazine in rainfall samples from Isle Royale National Park, Michigan, as determined by ELISA and SPE-ELISA. Detection limit 0.005 µg/L.

Figure 3. Concentration of atrazine in soil-water samples collected from a lysimeter near Wallace Lake, Isle Royale National Park, Michigan. Concentrations determined by SPE-ELISA. Detection limit 5 ng/L.
Atrazine Concentrations in Surface Water

Surface, inflow, and outflow samples collected from Lake Richie and Wallace Lake had concentrations that ranged from 5 to 15 ng/L. In August of 1992, a survey of major lakes across Isle Royale (Fig. 1) revealed atrazine concentrations similar to those identified earlier in the season at the two field sites. Average concentrations ranged from 3.6 to 13.2 ng/L (nanograms per liter). Concentrations of atrazine in surface water collected during the August 1992 lake survey are listed in table 1.

CONCLUSIONS

Results from this study indicate that atrazine is capable of being transported atmospherically and deposited in significant amounts onto pristine areas. Once deposited on pristine areas, atrazine is detectable in surface water. The probable methods of transport include atrazine-laden precipitation falling directly onto lakes, surface runoff of atrazine-contaminated rainfall flowing into lakes, and possibly even ground-water inflow into lakes. Atrazine persisted in the lakes of Isle Royale at least several months after deposition by precipitation. Furthermore, the concentrations of atrazine in surface water did not decrease from the time of deposition (June) through August. This slow degradation of atrazine in surface water indicates that the mass of atrazine in the aquatic system may increase from year to year. Thus, ecosystems not affected by atrazine at this time should be evaluated to determine the risk to the systems if accumulation should occur. Finally, future studies may consider the inclusion of analysis for persistent metabolites of atrazine, such as deethylatrazine and deisopropylatrazine, in surface and soil water and to determine the amount and fate of these important compounds in the aquatic system. Also the discovery of cyanazine in the rainfall warrants an additional study of the amount of this toxic compound and it's metabolites being transported atmospherically as well as its fate in the pristine watershed.

REFERENCES CITED

Annual Use and Transport of Agricultural Chemicals in the Mississippi River, 1991-92

By William A. Battaglin¹, Donald A. Goolsby¹, and Richard H. Coupe²

Abstract

The presence of agricultural chemicals (herbicides, insecticides, and nutrients) in the Mississippi River and several tributaries follows an annual cycle. Herbicide concentrations are generally highest during periods of storm runoff following application in the spring and early summer. Nitrate concentrations are generally highest in the winter and spring and lower during the summer and fall.

Concentrations and mass transport of agricultural chemicals in rivers are generally related to the amounts of the chemicals used within the river drainage basins. A geographic information system (GIS) was used to analyze relations among county-level estimates of the mass of agricultural chemicals applied (kilograms of active ingredient applied per county) and the annual transport of dissolved chemicals in rivers. Relations were studied for the Mississippi River and several tributaries in the midwestern United States. County-level estimates of herbicide and nitrogen use were developed into a series of GIS data layers and used to estimate the mass of agricultural chemicals used annually within specific drainage basins. Analytical data from periodic water-quality sampling and daily streamflow data were used to estimate the mass of agricultural chemicals transported out of specific drainage basins by rivers. These data sets were used to develop statistical models for estimating annual transport of agricultural chemical as a percentage of estimated annual agricultural chemical use in the basins of the Mississippi River and several tributaries. Results indicated that, in 1991, estimated masses equivalent to about 15 percent of the commercial nitrogen fertilizer, 1.6 percent of the atrazine and cyanazine, 0.8 percent of metolachlor, and 0.2 percent of the alachlor applied in the drainage basins studied were transported out of the basins by rivers.

INTRODUCTION

The U.S. Geological Survey presently (1993) is conducting studies to determine the distribution, transport, and persistence of selected agricultural chemicals (herbicides, insecticides, and inorganic nutrients) in the Mississippi River and several tributaries. Previous studies indicated that transport of agricultural chemicals in runoff to streams is seasonal; the largest contributions occur during periods of late spring and early summer runoff (Baker and Richards, 1990; Goolsby and others, 1991a; Thurman and others, 1991; Goolsby and others, 1991b; Thurman and others, 1992; Goolsby and Battaglin, in press). These studies also indicate that agricultural chemicals are present in surface waters in concentrations that exceed Federal health-based levels for drinking water at certain times of the year (U.S. Environmental Protection Agency, 1992). However, these high concentrations generally do not persist throughout the year, and the health-based levels are based on average annual concentrations, not concentrations of short-duration (Goolsby and Battaglin, in press).

The Mississippi River Basin contains some of the most productive cropland in the world (Spalding and Exner, 1991). Agricultural chemicals are used extensively in this region to increase yields of agricul-

¹U.S. Geological Survey, WRD, MS-406, Denver, Colo. 80225
tural crops. In the Mississippi River Basin, an estimated 20,600 metric tons of atrazine, 18,500 metric tons of alachlor, 15,800 metric tons of metolachlor, 8,170 metric tons of cyanazine, and 6,263,000 metric tons of nitrogen fertilizer are used annually (Gianessi and Puffer, 1991; U.S. Environmental Protection Agency, 1990). Agricultural chemical use in the Mississippi River Basin accounts for more than one-half of the total use in the United States (Gianessi and Puffer, 1991; U.S. Environmental Protection Agency, 1990). Most of this agricultural chemical use is associated with the production of corn, soybeans, sorghum, and wheat.

Many agricultural chemicals are partially soluble in water and have the potential to leach to ground water or to run off to surface water. The presence of agricultural chemicals in surface waters of the midwestern United States is of concern because approximately 18 million people in the midwestern United States depend on the Ohio, Missouri, and Mississippi rivers and their tributaries for drinking-water supply (Howard Perlman, U.S. Geological Survey, written commun., 1991). Conventional water-treatment practices do not remove most of these agricultural chemicals, and costly alternative treatment methods, such as carbon filtration or denitrification, might be required to treat waters that do not meet health-based limits (U.S. Environmental Protection Agency, 1989; Adams and others, 1990; Madison and Brunett, 1985). An improved understanding of the spatial and temporal distribution agricultural chemicals in midwestern rivers is needed so that water-managers and suppliers can address the problems resulting from agricultural chemical contamination of water supplies.

The purposes of this paper are to (1) describe the methods used to estimate agricultural-chemical transport in the Mississippi River and several of its tributaries, and agricultural chemical use within the drainage basins associated with specific sampling points; and (2) present the results of simple statistical models that were used to estimate the annual dissolved transport of agricultural chemicals as a percentage of the estimated annual use of those chemicals. The results presented in this paper are for a particular year; the effects of climatic conditions and other factors that might change from year to year have on results are not addressed in this paper.

Eight large basins with drainage areas of 29,400 to 2,914,000 km$^2$ (fig. 1) were studied. The Mississippi River was sampled at three locations, and the Missouri, Ohio, Platte, Illinois, and White Rivers were each sampled at one location (fig. 1). All these river basins are predominantly within the corn and soybean producing region of the mid-continental United States.

**METHODS OF INVESTIGATION**

Streamflow from the eight basins was sampled periodically from April 1991 through March 1992. Except for the Ohio River, all sites were sampled every 3 to 4 days during May through mid-July, once per week during the remainder of the summer and fall, and once every 2 weeks during winter. The Ohio River was sampled once per week, except during winter when samples were collected every 2 weeks (Goolsby and others, 1991b). Samples were collected by depth-width integrating methods (Edwards and Glysson, 1988) and composited in stainless steel or glass containers. Samples for pesticide analysis were filtered through 0.7-μm pore-diameter glass-fiber filters into pre-cleaned glass bottles. Samples for nitrate analysis were filtered through 0.45-μm-membrane filters.

All samples from the eight basins were analyzed for herbicides by gas chromatography/mass spectrometry (GC/MS) following solid-phase extraction on C$_{18}$ cartridges (Sandstrom and others, 1991). Nitrite and nitrate plus nitrate concentrations for all sites were determined by automated colorimetric procedures (Fishman and Friedman, 1989). Nitrate concentration was calculated as the difference in concentration resulting from these two analytical determinations.

Daily dissolved transport of atrazine, alachlor, cyanazine, metolachlor, and nitrate as nitrogen was calculated for the eight basins as the product of measured or estimated daily concentrations and daily mean streamflow. Concentrations were estimated by linear interpolation on days when no samples were collected. The estimated daily transport was accumulated for the period April 1, 1991 to March 31, 1992, to obtain estimates of annual transport.

County-level herbicide use estimates were constructed by Gianessi and Puffer (1991) by -- (1) compiling statistics by State and by crop, on percentage of acres treated with a given herbicide and average annual application rate of the herbicide from surveys sent to Extension Service weed scientists in 1989 and 1987; (2) augmenting survey data with published surveys and reports from specific States (U.S. Department of Agriculture, 1989);
(3) establishing herbicide-use profiles, by State and by crop, containing the percentage of acres treated and average annual applications rates; 

(4) multiplying county-level crop acreage estimates from the 1987 Census of Agriculture (Bureau of the Census, 1989) by percentage of acres treated and average annual application rates to get herbicide use estimates; and 

(5) tabulating use of active ingredient of herbicides used by crop and by county.  
The total use of individual herbicides on all crops for each county was calculated prior to entering the herbicide-use estimates into the GIS. 

County-level nitrogen fertilizer sales for the 1991 fertilizer year (July 1, 1990 through June 30, 1991), were estimated (Gerald Fletcher, West Virginia University, written commun., 1992; U.S. Environmental Protection Agency, 1990). The fertilizer-sales estimates are reported as tons of actual nutrient (inorganic nitrogen, phosphate, and potash). The fertilizer sales estimates do not account for the use of manure. County-level nitrogen-fertilizer sales estimates were constructed by -- 

(1) compiling annual State fertilizer-sales data reported as tonnages to the National Fertilizer and
Environmental Research Center of the Tennessee Valley Authority;

(2) calculating the ratio of expenditures on commercial fertilizers by county to expenditures on commercial fertilizers by State from the 1987 Census of Agriculture (Bureau of the Census, 1989); and

(3) computing annual county-level fertilizer sales, in tons, by multiplying estimates of annual State sales by the ratio of county expenditures to State expenditures.

The county-level estimates of nitrogen-fertilizer sales in tons of actual nutrient were entered directly into the GIS.

An area-weighted transfer algorithm was programmed in the GIS and used to generate estimates of the masses of agricultural chemicals used within the drainage basins studied. The transfer algorithm accounts for cases where both the entire county is within a drainage basin, and where only a portion of a county is within a drainage basin. In the latter case, the value of the attribute being transferred is weighted by the ratio of the area of the county within the basin to the total county area. For example, if 25 percent of county X falls within basin Y, and atrazine use is estimated to have been 4,000 kg in county X, then 1,000 kg of atrazine from county X is transferred to basin Y.

USE AND TRANSPORT OF AGRICULTURAL CHEMICALS

Graphs of concentration for atrazine, alachlor, cyanazine, metolachlor, and nitrate in water samples collected at the sampling site on the Mississippi River at Thebes, Ill., (fig. 2) show the temporal patterns in agricultural-chemical concentrations that were observed at all eight sampling sites. The spring-flush phenomenon previously reported by Thurman and others (1991) is readily apparent. In the Mississippi River, concentrations change more slowly, peak concentrations are lower, and elevated concentrations are sustained for a longer period of time than they are in smaller streams. These differences can be attributed to the fact that these large rivers integrate the agricultural-chemical input from many smaller streams. The year-round occurrence of herbicides, such as atrazine, in the Mississippi River indicates that some agricultural chemicals are stored and subsequently released from surface-water and ground-water reservoirs (Goolsby and Battaglin, in press; Squillace and Thurman, 1992).

The estimates of annual agricultural chemical transport (table 1) represent only transport of dissolved chemicals. Earlier research by Pereira and Rostad (1990) indicated that 99.5 percent of the atrazine, cyanazine and metolachlor was in the dissolved phase and less than 0.5 percent was in the suspended phase in the lower Mississippi River. Squillace and Thurman (1992) estimated that 1 percent or less of the total atrazine was present in the suspended phase in samples from the Cedar River in Iowa. The estimates of annual transport of agricultural chemicals in the Mississippi River are similar to those reported by Goolsby and others (1991) but significantly larger than those reported by Pereira and others (1989).

Graphics showing the relative intensity of agricultural-chemical use were created to help visualize the spatial distribution of agricultural chemical use across the United States. Examples of the herbicide and nitrogen-fertilizer use data are shown in figure 3. For these examples, county-level estimates of atrazine use, in kilograms, or nitrogen-fertilizer use, in metric tons, have been divided by county land area. A statistical distribution was used to select six class intervals for the graphic displays of agricultural chemical use. The empty (white) class represents counties where data on agricultural-chemical use are missing or zero. The first shaded class (lightest grey) represents use data that are greater than zero and as large as the 25th percentile of the data, the second grey-shaded class represents use data that are greater than the 25th percentile and as large as the median of the data, the third grey-shaded class represents use data that are greater than the median and as large as the 75th percentile of the data, the fourth grey-shaded class represents use data that are greater than the 75th percentile and as large as the 75th percentile plus two standard deviations of the data, and the fifth grey-shaded class represents use data that are greater than the 75th percentile and as large as the 75th percentile plus two standard deviations.

Linear regressions were used to investigate relations between estimates of agricultural chemical transport (table 1) and use (table 2), and to estimate transport of agricultural chemicals as a percentage of estimated annual agricultural-chemical use. For the Mississippi River and several tributaries, significant relations (p < 0.05) were determined when estimates of annual transport were regressed with estimates of
Figure 2. Temporal distribution of (a) herbicides: Atrazine, alachlor, cyanazine, and metolachlor concentrations (b) nitrogen concentration, and (c) discharge in the Mississippi River at Thebes, Illinois.
Table 1.--Estimated transport of atrazine, alachlor, cyanazine, metolachlor, and nitrate in metric tons, by the Mississippi River and several tributaries, April 1991 through March 1992

<table>
<thead>
<tr>
<th>Sampling station name</th>
<th>Atrazine</th>
<th>Alachlor</th>
<th>Cyanazine</th>
<th>Metolachlor</th>
<th>Nitrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mississippi at Baton Rouge, La.</td>
<td>321.</td>
<td>33.7</td>
<td>127.</td>
<td>123.</td>
<td>967,000</td>
</tr>
<tr>
<td>Mississippi at Thebes, Ill.</td>
<td>189.</td>
<td>42.9</td>
<td>113.</td>
<td>87.2</td>
<td>651,000</td>
</tr>
<tr>
<td>Missouri River at Hermann, Mo.</td>
<td>68.4</td>
<td>7.87</td>
<td>31.3</td>
<td>24.7</td>
<td>79,900</td>
</tr>
<tr>
<td>Ohio River at Grand Chain, Ill.</td>
<td>57.0</td>
<td>4.97</td>
<td>13.4</td>
<td>20.2</td>
<td>182,000</td>
</tr>
<tr>
<td>Mississippi River at Clinton, Iowa</td>
<td>15.1</td>
<td>5.64</td>
<td>8.94</td>
<td>8.10</td>
<td>157,000</td>
</tr>
<tr>
<td>Platte River at Louisville, Nebr.</td>
<td>9.28</td>
<td>2.35</td>
<td>5.91</td>
<td>2.47</td>
<td>5,640</td>
</tr>
<tr>
<td>Illinois River at Valley City, Ill.</td>
<td>35.8</td>
<td>8.79</td>
<td>19.8</td>
<td>18.9</td>
<td>107,000</td>
</tr>
<tr>
<td>White River at Hazelton, In.</td>
<td>5.68</td>
<td>1.04</td>
<td>1.71</td>
<td>2.11</td>
<td>11,500</td>
</tr>
</tbody>
</table>

Annual use for atrazine, alachlor, cyanazine, metolachlor, and nitrate as N (table 3). The regressions with alachlor and nitrate do not appear to fit well at the smaller values of transport and use (fig. 4). However, there are other sources of nitrogen besides chemical fertilizers, such as domestic and animal wastes, legumes, and natural sources that are not accounted for in the use term of the nitrate regression equation.

Values for the Pearson's product-moment correlation coefficient (Davis, 1986), multiple R-square, P(F) value, and slope of the regression line for the regressions equations are given in table 3. Both agricultural-chemical transport and use are highly correlated to basin area, which could inflate the goodness of fit statistics in table 3. Also, the Mississippi River at Baton Rouge site has a strong influence on all of the regressions because this site represents the largest drainage area (fig. 4).

Estimates of annual agricultural chemical transport as a percentage of estimated annual use for the eight drainage basins are shown in table 4. The results in tables 3 and 4 indicate that, on an annual basis, estimated masses equivalent to about 15 percent of the commercial fertilizer, 1.6 percent of the atrazine and cyanazine, 0.8 percent of metolachlor, and 0.2 of the alachlor used in large drainage basins in the midwestern United States are transported out of the basins by rivers. However, table 4 indicates that there is significant basin-to-basin variability in the estimates of transport as a percentage of use. The maximum values of all herbicide transport as a percentage of use are for the Illinois River. The estimates of chemical transport as a percentage of estimated annual use for cyanazine are likely to be smaller than those listed in table 4, since cyanazine use estimates were constructed using 1989 data, and the manufacturer of cyanazine reports a 24.3 percent increase in cyanazine sales between 1989 and 1991 (Patti Tillotson, DuPont Agricultural Products, written comm., 1993).

Previous investigations have demonstrated a relation between herbicide use and time-weighted mean herbicide concentrations (Baker and Richards, 1990) and between herbicide use and transport (Hall and others, 1972; Squillace and Thurman, 1992). Wauchope (1978) summarized the results of several studies investigating the loss (transport from field to stream) of herbicides from agricultural areas and proposed numbers representing expected herbicide losses as a percentage of use that could be useful for water-quality planning for large regions. The results...
Figure 3. Estimated county-level: (a) atrazine use; (b) nitrogen fertilizer use, July 1, 1990, to June 30, 1991.
Table 2.--Estimated annual application of atrazine, alachlor, cyanazine, metolachlor, and nitrogen as commercial fertilizer in metric tons, in the Mississippi and several tributary basins

<table>
<thead>
<tr>
<th>Sampling station name</th>
<th>Upstream drainage area in square kilometers</th>
<th>Estimated application, in metric tons</th>
<th>Atrazine</th>
<th>Alachlor</th>
<th>Cyanazine</th>
<th>Metolachlor</th>
<th>Nitrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mississippi at Baton Rouge, La.</td>
<td>2,914,000</td>
<td>18,500</td>
<td>20,600</td>
<td>15,800</td>
<td>6,263,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mississippi at Thebes, Ill.</td>
<td>1,847,000</td>
<td>13,400</td>
<td>12,200</td>
<td>11,000</td>
<td>4,055,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Missouri River at Hermann, Mo.</td>
<td>1,357,000</td>
<td>6,280</td>
<td>4,660</td>
<td>3,490</td>
<td>1,930,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ohio River at Grand Chain, Ill.</td>
<td>526,000</td>
<td>5,060</td>
<td>4,900</td>
<td>3,440</td>
<td>1,133,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mississippi River at Clinton, Iowa</td>
<td>222,000</td>
<td>1,440</td>
<td>2,040</td>
<td>1,630</td>
<td>607,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Platte River at Louisville, Nebr.</td>
<td>222,000</td>
<td>1,600</td>
<td>1,030</td>
<td>464</td>
<td>444</td>
<td>425,000</td>
<td></td>
</tr>
<tr>
<td>Illinois River at Valley City, Ill.</td>
<td>69,000</td>
<td>1,960</td>
<td>1,880</td>
<td>715</td>
<td>1,760</td>
<td>450,000</td>
<td></td>
</tr>
<tr>
<td>White River at Hazelton, In.</td>
<td>29,000</td>
<td>711</td>
<td>851</td>
<td>214</td>
<td>424</td>
<td>143,000</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.--Goodness of fit statistics for regression relations of agricultural chemical transport, April 1991 through March 1992, with annual use

<table>
<thead>
<tr>
<th></th>
<th>Atrazine</th>
<th>Alachlor</th>
<th>Cyanazine</th>
<th>Metolachlor</th>
<th>Nitrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pearson product-moment correlation coefficient</td>
<td>0.994</td>
<td>0.889</td>
<td>0.983</td>
<td>0.997</td>
<td>0.968</td>
</tr>
<tr>
<td>Multiple R-square</td>
<td>0.989</td>
<td>0.790</td>
<td>0.967</td>
<td>0.994</td>
<td>0.936</td>
</tr>
<tr>
<td>P(F)-value</td>
<td>0.0000</td>
<td>0.0032</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0001</td>
</tr>
<tr>
<td>Slope of regression line</td>
<td>1.56</td>
<td>0.22</td>
<td>1.68</td>
<td>0.79</td>
<td>15.47</td>
</tr>
</tbody>
</table>

from this study can be compared with results from these other studies. Hall and others (1972) estimated atrazine transport in runoff water was 2 percent of the amount applied at the recommended rate. Squillace and Thurman (1992) estimated that 1.5 to 5 percent of the atrazine applied was transported from the Cedar River basin in 1984. Wauchope (1978) estimated that 2 to 5 percent of herbicides applied as wettable powders (includes atrazine and cyanazine) and 1 percent of other herbicides (including alachlor), were lost in runoff. The results of the present study indicate slightly smaller loss of herbicides than estimated by Wauchope (1978) and Hall and others (1972). The difference could be the result of basin-to-basin variability, climatic conditions particular to the year of study, or changing agricultural management systems.
Figure 4. Graphs showing agricultural chemical transport as a function of use in the Mississippi River and several tributaries for: (a) atrazine, (b) alachlor, (c) cyanazine, (d) metolachlor and (e) nitrate.

NOTE: The estimates of cyanazine use are likely to be larger than shown on this graph, since use estimates are constructed using 1989 data, and the manufacturer of cyanazine reports a 24.3 percent increase in cyanazine sales between 1989 and 1991 (Patti Tillotson, DuPont Agricultural Products, written commun., 1993)
Estimates of agricultural chemical use compiled using a GIS and estimates of agricultural chemical transport calculated from periodic water-quality sampling and daily mean stream flow data were compared using linear regression models for the Mississippi River and several tributaries in the midwestern United States. Results indicated that, during April 1991 through March 1992, as a percentage of use for atrazine, alachlor, cyanazine, metolachlor, and nitrate, in the Mississippi River and several tributaries.

### Table 4

<table>
<thead>
<tr>
<th>Sampling station same</th>
<th>Atrazine</th>
<th>Alachlor</th>
<th>Cyanazine</th>
<th>Metolachlor</th>
<th>Nitrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mississippi at Baton Rouge, La.</td>
<td>1.56</td>
<td>0.18</td>
<td>1.55</td>
<td>0.78</td>
<td>15.44</td>
</tr>
<tr>
<td>Mississippi at Thebes, Ill.</td>
<td>1.41</td>
<td>0.35</td>
<td>1.82</td>
<td>0.79</td>
<td>16.05</td>
</tr>
<tr>
<td>Missouri River at Hermann, Mo.</td>
<td>1.09</td>
<td>0.17</td>
<td>1.59</td>
<td>0.71</td>
<td>4.14</td>
</tr>
<tr>
<td>Ohio River at Grand Chain, Ill.</td>
<td>1.13</td>
<td>0.10</td>
<td>0.93</td>
<td>0.59</td>
<td>16.06</td>
</tr>
<tr>
<td>Mississippi River at Clinton, Iowa</td>
<td>1.05</td>
<td>0.28</td>
<td>0.56</td>
<td>0.50</td>
<td>25.86</td>
</tr>
<tr>
<td>Platte River at Louisville, Nebr.</td>
<td>0.58</td>
<td>0.23</td>
<td>1.27</td>
<td>0.57</td>
<td>1.33</td>
</tr>
<tr>
<td>Illinois River at Valley City, Ill.</td>
<td>1.83</td>
<td>0.47</td>
<td>2.77</td>
<td>1.07</td>
<td>23.78</td>
</tr>
<tr>
<td>White River at Hazelton, In.</td>
<td>0.80</td>
<td>0.12</td>
<td>0.80</td>
<td>0.50</td>
<td>8.04</td>
</tr>
</tbody>
</table>

Value from regression of transport with use, all basins: 1.56, 0.22, 1.68, 0.79, 15.47

Possible causes of variations in nitrate transport from east to west include differences in agricultural practices, population density, climatic conditions, and surficial materials. These possible causes need to be tested in future studies. The strength of the relations between agricultural chemical use and agricultural chemical transport (table 3) indicates that rates of chemical use could be as important in determining regional vulnerability to surface-water contamination as other hydrogeological factors, such as aquifer type, soil type, and agricultural management systems.

### SUMMARY

Estimates of agricultural chemical use and transport calculated from periodic water-quality sampling and daily mean stream flow data were compared using linear regression models for the Mississippi River and several of its tributaries in the midwestern United States. Results indicated that, during April...
1991 thorough March 1992, estimated masses equivalent to about 15 percent of the commercial fertilizer, 1.6 percent of the atrazine and cyanazine, 0.8 percent of metolachlor, and 0.2 of the alachlor used in the basins were transported in the dissolved phase out of the basins by rivers.

REFERENCES


U.S. Environmental Protection Agency, 1990, County-level fertilizer sales data: Office of Policy, Planning, and Evaluation (pm-221).


Relation of Nitrate Concentrations in Surface Water to Land Use in the Upper-Midwestern United States, 1989-90

By David K. Mueller¹, Barbara C. Ruddy¹, and William A. Battaglin¹

Abstract

As part of a study on contamination from agricultural chemicals, nitrate data were collected during several synoptic surveys at a large number of surface-water sites in 10 midwestern states during 1989-90. These data were analyzed using logistic regression to relate discrete categories of nitrate concentrations to land use in the drainage basins upstream from the sampling sites. The nitrate data were divided into three categories representing background concentrations, elevated concentrations, and concentrations that exceeded the U.S. Environmental Protection Agency maximum contaminant level for drinking water. Land-use data were derived from spatial-digital data available from several sources in national data bases. The explanatory variables selected for the best-fit model were percentile of streamflow at the time of sampling, acreage of the basin in corn, acreage in soybeans, density of cattle, and population density. All these variables have qualitative relations to nitrate sources, mobilization, or transport. Classification of nitrate categories from this model was 80 percent accurate in comparison to observed categories. The accuracy of the model was better for classification into categories that represented lower concentrations; however, incorrect classifications were not biased either high or low. Results from this study indicate that land-use data can be useful in analyses of water-quality conditions in large regions and that logistic regression is a valuable technique for use in such analyses.

¹U.S. Geological Survey, Lakewood, CO.

INTRODUCTION

Large quantities of agricultural chemicals, including herbicides and nitrogen fertilizers are applied each year to farmland in the upper-midwestern United States. These applications, in conjunction with the moderately large solubility and mobility of some herbicides and nitrate, create the possibility for substantial contamination of surface and ground water. In 1989, the U.S. Geological Survey (USGS) began a regional study of herbicides and nitrate in surface waters of a 10-State area (fig. 1). Synoptic sampling surveys were conducted in the spring and summer of 1989 and 1990 and in the fall of 1989. Analysis of regional synoptic data is an important aspect of several programs within the USGS, including the National Water Quality Assessment Program (NAWQA) and the Toxic Substances Hydrology Program. The results of herbicide analyses from these samples have been presented previously (Goolsby and others, 1991, Thurman and others, 1991).

This paper presents results of the nitrate-data analysis -- specifically, the concept that nitrate concentrations in the synoptic samples are related to land-use data derived from large-scale geographic data bases. Also, statistical models that can be used to estimate nitrate concentrations from land-use data are evaluated.

SOURCE OF DATA

Surface-water samples were collected at 141 sites in Illinois, Indiana, Iowa, Kansas, Minnesota, Missouri, Ohio, Nebraska, South Dakota, and Wisconsin (fig. 1). Sampling sites were selected to be proportional to corn production in each State (D.A. Goolsby, U.S. Geological Survey, written commun., 1989, 1990). Within States, site selection was based
on geographic distribution and drainage-basin area. Most sites were located at existing USGS streamflow-gaging stations.

Samples were collected three times in 1989: (1) spring (March-May), before the application of herbicides, but not necessarily prior to application of nitrogen fertilizers; (2) summer (May-July), during the first major runoff event after application of herbicides; and (3) fall (October-November), after the first killing frost. Samples were analyzed for selected herbicides and for dissolved nitrite plus nitrate (herein-after referred to as nitrate). Field measurements of temperature, pH, and specific conductance were made and streamflow was either measured or derived from a rating curve.

Fifty sites were resampled during the spring and summer of 1990. Selection of these sites was based on ranking the samples collected during the summer of 1989 according to the total herbicide concentration. The sampling sites were divided into three equal groups. Twenty-five sampling sites were randomly selected from the group that contained the highest concentrations; 13 sampling sites were randomly selected from the group that contained the lowest concentrations. Two additional sampling sites were selected in northeast Iowa from basins that were not sampled in the summer of 1989 because of drought.

Geographic data for the study area were obtained from several sources. Agricultural data, including land use, crop types, and livestock, were collected for the 1987 Census of Agriculture (U.S. Bureau of Census, 1989). Data on nitrogen fertilizer sales during 1989 and 1990 were obtained from the U.S. Environmental Protection Agency (USEPA) (1990). Although these data are for sales, they were considered to represent fertilizer application as well. Population data were collected for the 1990 Census of Population and Housing (U.S. Bureau of Census, 1990). All data were retrieved from Geographic Information System (GIS) data bases, stored as 1:2,000,000-scale digital maps of the coterminous United States. The agricultural and fertilizer data were stored by county. The population data were stored by census geographic units (block groups).

Digital data extracted from these sources were used to compute values for the drainage basin...
upstream from each surface-water sampling site. A computerized GIS procedure was used to areally weight the extracted data and sum it by basin. When basins were nested (a large basin can contain several smaller basins), the data for the smaller basins were summed to derive the information for the large basin.

The final step in development of the data was to convert the basin data to units that were independent of basin size. For the geographic data, this conversion was done by dividing the data values by basin area. Streamflow at the time of sampling was converted to a percentile value on the basis of the flow-duration relation for daily streamflow at the site. Percentile of flow has been shown to be preferable to actual streamflow in making comparisons among basins of different sizes and, consequently, different flow regimes (D.R. Helsel, U.S. Geological Survey, written commun., 1993). Daily streamflow records were not available for five sampling sites; therefore, flow percentiles could not be computed and those basins were omitted from subsequent analyses. Also, one basin was omitted because no samples were collected during the spring or summer sampling periods in either 1989 or 1990. The resultant data set contained values for 135 basins, having drainage areas that ranged from 89 to about 19,000 mi² (square miles). The variables in this data set are listed in table 1.

### STATISTICAL METHODS

The initial attempt to relate nitrate concentrations at each site to land use in the upstream drainage basin was made by using multiple linear regression (MLR). However, no satisfactory MLR models were identified. Logistic regression was selected as an alternative method.

Logistic regression commonly is used when the response variable is discrete or categorical, rather than continuous (Helsel and Hirsch, 1992, p. 393). The logistic regression model is similar to the MLR model in that a set of explanatory variable is used to estimate the value of a response variable. The response variable

<table>
<thead>
<tr>
<th>Variable (attribute)</th>
<th>Units</th>
<th>Minimum</th>
<th>Median</th>
<th>Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dissolved nitrite plus nitrate, as nitrogen</td>
<td>mg/L</td>
<td>&lt;0.1</td>
<td>2.5</td>
<td>19</td>
</tr>
<tr>
<td>Percentile of flow</td>
<td>none</td>
<td>.5</td>
<td>67.5</td>
<td>99.5</td>
</tr>
<tr>
<td>Total harvested cropland</td>
<td>acre/mi²</td>
<td>57.1</td>
<td>345</td>
<td>480</td>
</tr>
<tr>
<td>Acreage in corn, including silage</td>
<td>acre/mi²</td>
<td>3.06</td>
<td>149</td>
<td>267</td>
</tr>
<tr>
<td>Acreage in soybeans</td>
<td>acre/mi²</td>
<td>.51</td>
<td>126</td>
<td>239</td>
</tr>
<tr>
<td>Acreage in grain (wheat, oats, and rye)</td>
<td>acre/mi²</td>
<td>1.69</td>
<td>15.9</td>
<td>192</td>
</tr>
<tr>
<td>Acreage in hay</td>
<td>acre/mi²</td>
<td>4.25</td>
<td>25.4</td>
<td>158</td>
</tr>
<tr>
<td>Pastureland, including pastured woodland</td>
<td>acre/mi²</td>
<td>6.04</td>
<td>49.4</td>
<td>397</td>
</tr>
<tr>
<td>Woodland, not pastured</td>
<td>acre/mi²</td>
<td>1.09</td>
<td>11.3</td>
<td>75.5</td>
</tr>
<tr>
<td>Cattle</td>
<td>number/mi²</td>
<td>5.09</td>
<td>55.3</td>
<td>176</td>
</tr>
<tr>
<td>Hogs</td>
<td>number/mi²</td>
<td>.99</td>
<td>98.3</td>
<td>448</td>
</tr>
<tr>
<td>Poultry (chickens and turkeys)</td>
<td>number/mi²</td>
<td>.05</td>
<td>32.3</td>
<td>6,280</td>
</tr>
<tr>
<td>Fertilizer application</td>
<td>ton N/mi²</td>
<td>1.38</td>
<td>14.3</td>
<td>27.2</td>
</tr>
<tr>
<td>Population density</td>
<td>number/mi²</td>
<td>1.58</td>
<td>32.8</td>
<td>1,960</td>
</tr>
</tbody>
</table>
in logistic regression is the log of the odds ratio, 
\[ \frac{p}{1-p} \], where \( p \) is the probability of a data value being 
in one of the possible categories (Helsel and Hirsch, 1992, p. 395-396). The logistic regression equation is
\[ \log \left( \frac{p}{1-p} \right) = b_0 + bX, \]
where, \( b_0 \) = the intercept, \( X \) = the vector of \( k \) explanatory variables, and \( b \) = the vector of slope coefficients 
for each explanatory variable, so that \( bX = b_1X_1 + b_2X_2 + \ldots + b_kX_k \).

The slope coefficients are fit to the categorical data by the method of maximum likelihood (Helsel and Hirsch, 1992, p. 397). This method optimizes the likelihood that the observed data will be estimated from a given set of slope coefficients.

To create a discrete variable, observed concentrations of nitrate (as nitrogen) in each sample were divided into three categories: less than 3 mg/L, 3 to 10 mg/L, and greater than 10 mg/L. A total of 359 samples from the 135 sites during four synoptic sampling periods (spring and summer, 1989 and 1990) were included in this data set. More than one-half of the observations (192) were in the first category, which was considered to include background concentrations of nitrate in the study area. Observations in the second category (138) were considered elevated but were less than the USEPA maximum contaminant level (MCL) of 10 mg/L for drinking water (U.S. Environmental Protection Agency, 1986). Observations in the third category (29) exceeded the MCL. The categorized nitrate data for samples collected during the spring and summer of 1989 are shown in figure 2.

Best-fit logistic regression models were selected to estimate nitrate concentrations from land-use data by using a stepwise procedure. Explanatory variables were added to the model in order of significance, if the significance level (p-value) of the slope coefficient was less than or equal to 0.15. As variables were added, previously entered variables could be removed if their p-values increased to greater than 0.20.

To decrease the possibility of collinearity (cross correlation among the independent variables), the list of explanatory variables used in model fitting was restricted. Fertilizer application and total cropland were strongly correlated with corn and soybean acreage; therefore, fitting procedures were applied to two sets of explanatory variable: one set included fertilizer and total cropland data, and the other included corn and soybean acreage data. All the other explanatory variables listed in table 1 were included in both sets. Slope coefficients were determined separately for spring and summer data. Separate coefficients also were determined for classification between the low (concentrations less than 3 mg/L) and medium (3 to 10 mg/L) nitrate categories and between the medium and high (greater than 10 mg/L) categories. Overall, four sets of coefficients were determined using the same selected group of explanatory variables. A model consisted of the selected variables and the four sets of coefficients.

Models were compared on the basis of their capability to classify nitrate concentrations correctly. First, the model was used to estimate the probabilities of nitrate concentrations being in a particular category for each sample. Estimated probabilities were computed for the same data set used to fit the model. The classified category was selected to be the one with the maximum probability. The accuracy of the model was determined by comparing the classified category to the observed category.

RESULTS AND DISCUSSION

Two best-fit models were selected—one from each set of explanatory variables. For the variable set that included fertilizer and total-cropland data but no data on individual crop types, the selected explanatory variables were percentile of flow, fertilizer application, and population density. The logistic regression fit to these explanatory variables is referred to as model 1 in this paper. Comparisons of nitrate categories estimated by model 1 to observed nitrate concentrations are listed in table 2. The overall accuracy of the model is determined by the total percentage of correct classifications. For model 1, 73 percent of the classifications were correct. However, only 34 percent of the observations greater than 10 mg/L were correctly classified. Also, model 1 might be biased because most of the incorrect classifications were low.

Model 2 was fitted by use of the set of explanatory variables that included crop types, but not fertilizer application or total cropland. The selected explanatory variables from this set were percentile of flow, acreage in corn, acreage in soybeans, cattle, and population density. Accuracy results for model 2 also are listed in table 2. The overall accuracy of correct classifications was 80 percent, which is a slight improvement over that of model 1. Most of this improvement was attributed to better accuracy in
Figure 2. Geographic distribution of concentrations of dissolved nitrite plus nitrate as nitrogen, in selected streams in the upper-midwestern United States, displayed by drainage basin, for samples collected during the spring and summer 1989.
Table 2. Observed nitrate categories and category classifications from the logistic regression models

[mg/L, milligrams per liter; --, not applicable]

<table>
<thead>
<tr>
<th>Category (mg/L)</th>
<th>Observed</th>
<th>Classified correct</th>
<th>Classified low</th>
<th>Classified high</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Number</td>
<td>Percent</td>
<td>Number</td>
</tr>
<tr>
<td>Model 1 (percentile of flow, fertilizer application, and population density)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>&lt;3</td>
<td>192</td>
<td>164</td>
<td>85</td>
<td>--</td>
</tr>
<tr>
<td>3-10</td>
<td>138</td>
<td>87</td>
<td>63</td>
<td>42</td>
</tr>
<tr>
<td>&gt;10</td>
<td>29</td>
<td>10</td>
<td>34</td>
<td>19</td>
</tr>
<tr>
<td>Total</td>
<td>359</td>
<td>261</td>
<td>73</td>
<td>61</td>
</tr>
</tbody>
</table>

Model 2 (percentile of flow, acreage in corn, acreage in soybeans, cattle, and population density)

|                |          |        |        |        |        |        |        |
| Model 2        |          |        |        |        |        |        |        |
| <3             | 192      | 166    | 86     | --     | --     | 26     | 14     |
| 3-10           | 138      | 104    | 75     | 27     | 20     | 7      | 5      |
| >10            | 29       | 16     | 55     | 13     | 45     | --     | --     |
| Total          | 359      | 286    | 80     | 40     | 11     | 33     | 9      |

Classifying the higher concentrations. Classifications from model 2 were correct for 75 percent of the observed nitrate concentrations in the medium (3 to 10 mg/L) category and for 55 percent of the observed nitrate concentrations in the high (greater than 10 mg/L) category. This accuracy is a substantial improvement over model 1. Also, the incorrect classifications were about evenly distributed between high and low values, so model 2 does not seem to be biased.

The spatial distribution of the classification accuracy using model 2 for data from the spring and summer of 1989 is shown in figure 3. Incorrect classifications, both low and high, are distributed in a relatively uniform pattern throughout the study area. This result indicates that the model classifications are not geographically biased. Therefore, the accuracy of the model does not seem to depend on correlation of the explanatory variables with regional geography.

Generally, model 2, which is based on crop-type data, is superior to model 1, which is based on fertilizer data. Model 2 also is reasonably accurate in categorizing nitrate concentrations in the outflow from a variety of basins on a regional and seasonal scale. Model classifications do not seem to be biased in either magnitude or geographic distribution. These results lead to two primary conclusions. First, the level of nitrate contamination in midwestern streams is most strongly related to streamflow and to several characteristics of the upstream basin, including the areal extent of corn and soybean production, the density of cattle, and the population density. This list seems logical because each variable has a qualitative relation to nitrate. Streamflow results from basin runoff, which provides the mechanism for mobilization and transport of nitrate. In the model, as the percentile of flow increases, the probability increases that nitrate concentration will be in a higher category. Corn and soybeans are the major crops in the region, and their extent in the basin logically should be related to the use of all fertilizers, including commercial fertilizers and manure. Cattle also could be related to fertilizer use because they are a primary source of manure. Perhaps if data were available on actual fertilizer application, rather than only on fertilizer sales, a better model based on fertilizer instead of crop-type and livestock data could be developed. Population density is related to outflow from sewage-treatment plants, which generally are point sources of nitrate or of ammonia (a nitrogen species that can readily oxidize to nitrate). Even
Figure 3. Accuracy of nitrate-concentration categories estimated from logistic model 2 based on comparison to concentrations in samples collected during the spring and summer of 1989.
in rural areas, population density likely is related to nitrate contamination from septic system leachate.

A second conclusion is that an adequate model can be developed by relating synoptic water-quality data to regionally derived geographic data. All the explanatory variables in the model were retrieved from large GIS data bases that had, at best, a county-scale resolution. Yet these data were adequate to classify 80 percent of the observed nitrate concentrations correctly in outflow from a variety of basins.

The implication of these conclusions is that land-use data can be used to analyze water-quality conditions within large regions. Reasonable models can be developed for relating water quality to land use. These models can be adequate, even if the land-use data are extracted from large-scale data bases. Refinement of the models might be possible by collecting more precise land-use data in the basins upstream from sampling sites. More precise explanatory data could improve the accuracy of model classifications. The models could be used to identify other basins in the region where surface-water contamination might be a problem. Models from different regions could be compared to identify similarities and differences in the land-use factors that affect water quality in the regions. Logistic regression is a valuable technique for the development of these models.

REFERENCES


Reconnaissance Data for Selected Herbicides and Two Atrazine Metabolites in Surface Water of the Midwestern United States: Chemical Analysis by Immunoassay and Gas Chromatography/Mass Spectrometry

By Elisabeth A. Scribner¹, E. Michael Thurman¹, and Donald A. Goolsby²

Abstract

Water-quality data were collected from 147 rivers and streams during 1989-90 for an assessment of selected preemergent herbicides and two atrazine metabolites in 10 Midwestern States. All water samples were collected by depth-integrating techniques at three to five locations across each stream. Sites were sampled three times in 1989: before application of herbicides, during the first major runoff after application of herbicides, and in the fall during a low-flow period when most of the streamflow was derived from ground water. About 50 sites were selected by a stratified random procedure and resampled for both pre-and post-application herbicide concentrations in 1990 to verify the 1989 analytical results. Laboratory analyses consisted of enzyme-linked immunosorbent assay (ELISA) with confirmation by gas chromatography/mass spectrometry (GC/MS). The data have been useful in (1) studying herbicide transport, (2) comparing the spatial distribution of the post-application concentrations of 11 herbicides and 2 atrazine metabolites (deethylatrazine and deisopropylatrazine) in streams and rivers at a regional scale, (3) examining the annual persistence of herbicides and their metabolites in surface water, and (4) assessing whether the two atrazine metabolites can be used as indicators of surface- and ground-water interaction.

INTRODUCTION

During 1987-89, about 136 million pounds per year of four major herbicides were applied in a 10-State region (table 1). The herbicides alachlor, atrazine, cyanazine, and metolachlor accounted for about 73 percent of the herbicides applied (Gianessi and Puffer, 1990). The intense use of these herbicides with their partial water solubility and mobility cause them to leach into ground water, to run off in surface water, as well as to be transported aerially and to occur in precipitation (Goolsby and others, 1990). Runoff from fields immediately after herbicide application substantially increases herbicide concentrations in streams and rivers as reflected by increased concentrations of these herbicides in the Mississippi River (Goolsby and others, 1991a). Potentially serious problems concerning nonpoint-source contamination of surface- and ground-water supplies are associated with this agricultural chemical use. Drinking-water quality also is affected because conventional water-treatment practices do not remove these herbicides because they are soluble (Goolsby and others, 1990).

This paper presents the water-quality data collected during the reconnaissance study of surface water in the midwestern United States. This paper (1) describes the occurrence, distribution, and concentrations of nitrite plus nitrate and selected preemergent herbicides and two metabolites, (2) describes the geographic and seasonal distribution of nitrite plus nitrate and commonly used herbicides in streams of different size throughout the 10-State area, and (3) examines the usefulness of a low-cost immunoassay analysis for determining herbicide concentrations in a regional-scale reconnaissance study (Goolsby and others, 1990). The study area includes the following states: Illinois, Indiana, Iowa, Kansas, Minnesota, Missouri, Nebraska, Ohio, South Dakota, and Wisconsin (fig. 1).
Table 1. Quantities of four major herbicides applied in 10 agricultural Midwestern States, 1987-89
[From Gianessi and Puffer, 1990; values shown are in millions of pounds of active ingredient per year]

<table>
<thead>
<tr>
<th>State</th>
<th>Alachlor</th>
<th>Atrazine</th>
<th>Cyanazine</th>
<th>Metolachlor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Illinois</td>
<td>8.0</td>
<td>8.5</td>
<td>3.1</td>
<td>8.1</td>
</tr>
<tr>
<td>Indiana</td>
<td>6.9</td>
<td>5.7</td>
<td>1.7</td>
<td>3.5</td>
</tr>
<tr>
<td>Iowa</td>
<td>6.4</td>
<td>5.6</td>
<td>3.7</td>
<td>8.5</td>
</tr>
<tr>
<td>Kansas</td>
<td>1.9</td>
<td>4.7</td>
<td>0.2</td>
<td>2.2</td>
</tr>
<tr>
<td>Minnesota</td>
<td>4.0</td>
<td>1.5</td>
<td>2.8</td>
<td>2.4</td>
</tr>
<tr>
<td>Missouri</td>
<td>1.8</td>
<td>3.1</td>
<td>1.2</td>
<td>1.6</td>
</tr>
<tr>
<td>Nebraska</td>
<td>3.8</td>
<td>7.1</td>
<td>1.8</td>
<td>1.9</td>
</tr>
<tr>
<td>Ohio</td>
<td>3.7</td>
<td>3.8</td>
<td>1.6</td>
<td>4.0</td>
</tr>
<tr>
<td>South Dakota</td>
<td>1.9</td>
<td>0.5</td>
<td>0.3</td>
<td>1.0</td>
</tr>
<tr>
<td>Wisconsin</td>
<td>1.3</td>
<td>2.7</td>
<td>1.7</td>
<td>1.4</td>
</tr>
<tr>
<td>Total</td>
<td>39.7</td>
<td>43.2</td>
<td>18.1</td>
<td>34.6</td>
</tr>
</tbody>
</table>

Total of four major herbicides: 135.6

METHODS

Sampling Design

The 147 sampling sites were selected at U.S. Geological Survey (USGS) streamflow-gaging stations by a stratified random-sampling procedure designed to ensure geographic distribution and regional-scale interpretation of the data. The number of sites per State was proportional to the amount of corn and soybean production in each state, and sites were chosen randomly by county. The drainage area of the hydrologic units in which streams were sampled ranged from 66 to more than 700,000 mi², with a median drainage area of 770 mi². Most of the streams were sampled three times in 1989: before application of herbicides (March or April); after application and during the first major runoff (May or June); and in the fall during a low-flow period (October or November) when most of the streamflow was derived from ground water.

One-third of the streams sampled in 1989 were resampled during 1990 before herbicide application (March or April) and after herbicide application (May or June). The streams sampled in 1989 were ranked from largest to smallest total herbicide concentrations; 50 percent of the streams sampled in 1990 were randomly selected from the upper one-third, 25 percent from the middle one-third, and 25 percent from the lower one-third of the streams according to the ranked concentration.

EXPLANATION

- SAMPLED 1989
- SAMPLED 1989-90
- BOUNDARY OF HYDROLOGIC UNIT
- RECONNAISSANCE SAMPLING SITE

Figure 1. Location of study area, hydrologic units, and sites sampled in 1989 and 1990, in the midwestern United States. (From Thurman and others, 1992, fig. 1A.)
Sample-Collection Techniques

All water samples were collected by depth-integrating techniques at three to five locations across each stream (Thurman and others, 1992). The herbicide samples were collected, composited in large glass containers, and filtered through 1-m pore diameter, glass-fiber filters into baked glass bottles for shipment to the laboratory.

Analytical Procedures

Measurements were made onsite for specific conductance and pH. Samples, preserved with mercuric chloride, were analyzed for nitrate plus nitrite at the National Water Quality Laboratory, Arvada, Colorado (Fishman and Friedman, 1989). Herbicides were analyzed by enzyme-linked immunosorbent assay (ELISA) at the USGS laboratory in Iowa City, Iowa (Goolsby and others, 1991b). Most samples were also analyzed by gas chromatography/mass spectrometry (GC/MS) at the USGS laboratory in Lawrence, Kansas. Solvents used for analyzing samples included pesticide-grade methanol, ethyl acetate, and isooctane. Deionized water was charcoal filtered and glass distilled prior to use. Internal quantitative standard solutions were prepared in methanol and phenanthrene-d10. Assay kits were used for the immunoassay analysis. The kits used polyclonal antibodies coated on the walls of polystyrene test tubes and an atrazine-enzyme conjugate prepared by covalently binding atrazine to horseradish peroxidase by a modified carbodiimide technique (Bushway and others, 1988). The immunoassay procedure is described by Goolsby and others (1991b).

HERBICIDE OCCURRENCE AND DISTRIBUTION

Analyses results indicate that large concentrations of herbicides were flushed from cropland and transported through the surface-water system in response to late spring and early summer rainfall. Of the 10 herbicides and metabolites analyzed, atrazine, alachlor, metolachlor, and cyanazine were present in the largest concentrations. During the 1989 post-application sampling period, atrazine was detected in water samples from 98 percent of the stream sites. Alachlor, metolachlor, and deethylatrazine, an atrazine metabolite, were detected in water from more than 80 percent of the stream sites, and cyanazine was detected in water samples from more than 60 percent of the stream sites. Herbicide concentrations during the post-application period generally were larger than those measured before application and in the fall during low streamflow. The median concentration of atrazine during the post-application period was 3.8 μg/L compared with about 0.2 μg/L during the pre-application and fall low-flow periods. Similar seasonal distributions were observed for the other major herbicides (table 2).

During the late spring and summer, concentrations of one or more herbicides exceeded U.S. Environmental Protection Agency (USEPA) Proposed Maximum Contaminant Levels (PMCL) or lifetime Health Advisories Levels (HAL) for drinking water (U.S. Environmental Protection Agency, 1988; Federal Register, 1989, 1990) in more than one-half of the streams sampled. On the basis of results from storm-runoff samples collected in 1990, concentrations of some herbicides exceeded PMCLs during runoff for periods of several weeks to several months after application.

Analysis results indicate that atrazine was the most frequently detected and the most persistent of the major herbicides, followed by deethylatrazine and metolachlor. Alachlor and cyanazine were detected primarily during the late spring and summer. Atrazine was detected in three-fourths of the streams sampled during the fall, indicating that aquifers contributing base flow to the streams are contaminated by herbicides. Resampling of about 50 streams in 1990 before and after herbicide application produced results similar to those obtained in 1989. These results indicate an annual cycle of herbicide application followed by a series of flushing events during which herbicides are transported into streams and ground water, and by periods of base flow during which persistent herbicides in ground water slowly reenter the streams.

These are significant findings because they indicate that some of the parent herbicides persist from year to year in soil and water. Degradation products, such as deethylatrazine, are both persistent and mobile, and the data suggest that the ratio of deethylatrazine to atrazine (called the DAR), which has been used as an indicator of nonpoint-source contamination of ground water, may be used also to trace ground-water discharge into rivers.
Adams and Thurman (1991) found that DAR values for atrazine transport through the unsaturated zone were larger than 1.0, whereas DAR values for atrazine transported off the field by surface runoff were much less than 1.0. Thus, the magnitude of the DAR may be indicative of ground-water recharge by atrazine-laden water.

The ELISA data indicate that water samples from 55 percent of the streams in the hydrologic units studied exceeded the USEPA Maximum Contaminant Level (MCL) for atrazine in drinking water during the post-application sampling in 1989. It is important to note that ELISA cross reacts with ametryn, prometon, prometryn, propazine, simazine, and terbutryn, to a varying degree, but not with cyanazine and the degradation products of atrazine at the concentrations typically found in water samples (Thurman and others, 1990). The GC/MS data indicate that cyanazine and deethylatrazine frequently were detected along with trace concentrations of propazine and simazine, but there were no detections of ametryn, prometon, prometryn or terbutryn. In fact, atrazine was detected in 98 percent of the post-application stream water samples. The reporting limit of the ELISA method was set at 0.20 μg/L. At this concentration, neither false-positive nor false-negative detections were found. The ELISA correlation with GC/MS was good, with a correlation ($r^2$) of 0.86 using a simple regression with a nonliner fit for 127 surface-water samples. The difference between the measured and projected concentrations was less than 0.15 μg/L for 50 percent of the water samples and less than 0.8 μg/L for 80 percent of the samples. Thus, ELISA is a viable method for triazine surveys of surface water, ground water, and precipitation in the Midwest.

### SUMMARY

The results of this reconnaissance study indicate that runoff clearly has a regional effect on water quality after spring application of herbicides. This study also indicates that more needs to be learned about the duration of large herbicide concentrations in streams during periods of storm runoff and the possible implications of storing this water in reservoirs for long-term use. Furthermore, the large number of water samples in which a herbicide MCL was exceeded reinforces the need for environmental health studies to examine the combined and synergistic effects of the major herbicides and their degradation products. Finally, future studies should investigate the persistent degradation products of herbicides, such as deethylatrazine and deisopropylatrazine, and their role as hydrologic tracers in studies of the interaction of surface water and ground water.
REFERENCES CITED


Abstract

Deethylatrazine and deisopropylatrazine are two major metabolites of the triazine herbicides that occur in surface water of the midwestern United States. They may originate from the decomposition of several original parent compounds. Atrazine, the major triazine herbicide used in the Midwest, degrades systematically to both deethylatrazine and deisopropylatrazine with a ratio of approximately 0.40 for runoff water from cornfields. Ground water usually contains only trace concentrations of deisopropylatrazine compared to deethylatrazine because of the more rapid decomposition of deisopropylatrazine in the unsaturated zone. Thus, the deisopropylatrazine-to-deethylatrazine ratio ($D_2R$) may be used to distinguish surface-water runoff from ground water that discharges to surface water. However, other parent herbicides may affect the $D_2R$. For example, cyanazine may degrade to deisopropylatrazine by the loss of the cyano-isopropyl group. Because cyanazine is the fourth most frequently used herbicide in the Midwest, the $D_2R$ in surface water often is considerably greater than 0.40 (from 0.60-0.80). Simazine, another parent triazine herbicide, also may degrade to deisopropylatrazine. Simazine is used for weed control along highways and in orchards where considerably larger concentrations are applied. The resulting runoff contains deisopropylatrazine as a major dealkylated degradation product. Propazine, a parent triazine herbicide that is used only occasionally on grain sorghum, degrades to yield the deethylatrazine metabolite. Finally, terbuthylazine, a triazine not marketed in the United States, but used extensively in Europe, also may degrade to deisopropylatrazine via the loss of a t-butyl group. Thus, these parent compounds should be considered when using metabolite ratios as indicators of flow path.

INTRODUCTION

Agricultural practices may cause widespread degradation of water quality in the midwestern United States (Humenik and others, 1987; Thurman and others 1991; 1992). Approximately three-fourths of all pre-emergent herbicides used in the United States are applied to row crops in a 10-State area, called "the Corn Belt" (Gianessi and Puffer, 1986). Because herbicides are water soluble, there is the potential for leaching into surface and ground water (Hallberg, 1989; Thurman and others, 1991), as well as aerial transport and occurrence in precipitation (Glotfelty and others, 1983; Richards and others, 1987). Monitoring studies in the Midwest have shown widespread detection of herbicides and their metabolites in ground water (Hallberg, 1989) and in surface water (Wauchope and others, 1978; Glotfelty and others, 1984; Leonard, 1988; Pereira and Rostad, 1990; Thurman and others, 1991; 1992). Runoff from fields immediately after herbicide application substantially increases herbicide concentrations in streams that eventually are reflected in elevated concentrations in rivers, such as the Mississippi (Pereira and Rostad, 1990). Furthermore, conventional water-treatment practices do not remove these herbicides (Kearney and others, 1988; Miltner and others, 1989), which then can occur in drinking water.

In spite of these problems, the use of herbicides is required for successful farming, and elimination of herbicide use would create an economic hardship to farmers. Thus, it is important to understand the effects
of herbicides on water quality. An approach to understanding the effects of herbicides on water quality is to identify molecules as tracers of surface- and ground-water flow. A possible set of tracers is the two major dealkylated metabolites of triazine herbicides, deethylatrazine and deisopropylatrazine. The concentrations of these two compounds may be compared to the parent herbicide or to each other as ratios. These ratios include the deethylatrazine-to-atrazine ratio (DAR) and the deisopropylatrazine-to-deethylatrazine ratio (D2R).

The objective of the research described herein was to examine herbicide metabolites as tracers of surface- and ground-water flow. The specific objectives were to: (1) review previous work on the amounts of herbicides and dealkylated metabolites in the spring flush of streams on a regional scale and to examine the persistence of these metabolites in surface water, (2) illustrate how the parent herbicides may degrade to deethylatrazine and deisopropylatrazine, the major dealkylated metabolites of several important triazine herbicides, and (3) hypothesize how metabolites of atrazine may be used as indicators of surface- and ground-water interactions.

Figure 1. Location of stream-sampling sites in the midwestern United States.

DESCRIPTION OF STUDY AREA AND SAMPLE COLLECTION

Water samples were collected at 149 sites in 122 river basins in a 10-state area during three time periods (fig. 1). These states include: Illinois, Indiana, Iowa, Kansas, Minnesota, Missouri, Nebraska, Ohio, South Dakota, and Wisconsin. Water samples were collected during March and April (pre-planting), May and June (post-planting), and October and November (harvest) of 1989 at U.S. Geological Survey streamflow-gaging stations. One-third of the sites were resampled during 1990 at pre-planting and post-planting times. A stratified random-sampling procedure was used to ensure geographic distribution. Drainage areas of the selected basins ranged from 260 km² to more than 160,000 km², and, collectively, the basins drained more than 500,000 km² of the Midwest (fig. 1).

All water samples from the reconnaissance were collected by depth-integrating techniques from three to five locations across each stream. The samples were collected and composited in large glass containers and filtered through glass-fiber filters (1-micron pore
diameter) into baked glass bottles for shipment to the laboratory. The sampled drainage areas ranged from 200 to 5,000 km². All samples were analyzed for specific conductance, pH, nitrite plus nitrate, and triazine herbicides by enzyme-linked immunosorbent assay. Twenty-five percent of the samples were selected for analysis by gas chromatography/mass spectrometry (GC/MS).

**EXPERIMENTAL METHODS**

**Reagents and Supplies**

Methanol, ethyl acetate, and iso-octane were pesticide-grade solvents. Stock solutions of triazine herbicides and their deionized water were charcoal filtered and glass distilled prior to use. The C₁₈ (carbon-18) cartridges for solid-phase extraction contained 360 mg of 40 μm C₁₈-bonded silica. Standard solutions were prepared in methanol, and d₁₀ phenanthrene was used as an internal GC/MS quantification standard.

**Solid-Phase Extraction**

An automated workstation was used for solid-phase extraction (SPE) of the analytes. C₁₈ cartridges were preconditioned sequentially with 2 mL each of methanol, ethyl acetate, and distilled water. Each 10-mL water sample was spiked with a 100 mL of a surrogate standard, terbuthylazine (2.4 ng/mL), and pumped through a cartridge at a rate of 20 mL/min by robotic probe. Analytes were eluted with ethyl acetate and spiked automatically with d₁₀ phenanthrene (0.2 ng/μL, 500 μL). The ethyl-acetate layer was transferred automatically from a small co-eluted water layer to a centrifuge tube for nitrogen evaporation. The robotic probe was washed between samples by immersing in 4 mL of ethyl acetate and bubbling air through the probe to ensure thorough removal of any herbicide or spike residues adhering to the outside of the probe. Each sample required approximately 13 minutes for SPE. Finally, the extract was evaporated to 50 μL by a turbovap at 45 °C under a nitrogen stream.

**Analysis by Gas Chromatography/Mass Spectrometry**

Automated GC/MS analyses of the eluates were performed with a mass selective detector. Operating conditions were: ionization voltage, 70 electron volts; an ion-source temperature of 250 °C; electron multiplier, 2,200 volts; direct capillary interface at 280 °C, tuned daily with perfluorotributylamine; and a 50-millisecond dwell period. Separation of the herbicides was carried out using a fused-silica 12 m x 0.2 mm capillary column of methyl silicone with a film thickness of 0.33 μm. Helium was used as the carrier gas at a flow rate of 1 mL/min and a head pressure of 35 kPa. The column temperature was held at 50 °C for 1 minute, then ramped at 6 °C per minute to 250 °C, where it was held for 10 minutes. The injector temperature was 280 °C. The filament and multiplier were not turned on until 5 minutes into the analysis. Quantification of the base peak of each compound was based on the response of the 188 ion of the internal standard, d₁₀ phenanthrene. Confirmation of the molecular ion was based on the presence of two confirming ions with a retention time match of ±0.2 percent relative to d₁₀ phenanthrene.

**RESULTS AND DISCUSSION**

**Spring-Flush Phenomenon**

Atrazine was detected in 98 percent of the post-planting samples (table 1). The most striking feature of the reconnaissance data (table 1; fig. 2) was that large concentrations of herbicides were flushed from crop-lands and were transported through the surface-water system as pulses in response to late spring and early summer rainfall. The significance of the reconnaissance is that the pulse effect occurs at a regional scale throughout the midwestern United States and appears to be linked to regional agricultural land use. Herbicides are applied in the spring as a pre-emergent treatment. Fall application is minimal, and this fact is reflected by the small herbicide concentrations during the pre-planting sampling. Herbicide concentrations in only one basin exceeded U.S. Environmental Protection Agency Maximum Contaminant Levels (MCLs) for drinking water in the post-harvest samples. None of the pre-planting samples exceeded the MCLs.

Box plots of the GC/MS data from the three sampling periods are shown in figure 2. Median concentrations of the four major herbicides (alachlor, atrazine, cyazinamide, and metolachlor) increased by an order of magnitude, or more, from the pre-planting to the post-planting sampling periods, and then decreased to near pre-planting concentrations at the harvest sampling (fig. 2A, 2B). For example, the median concentration of atrazine during the post-planting period was 3.8 μg/L compared with 0.23 μg/L during the pre-planting and post-harvest periods. The total herbicide concentration, defined here as the sum of the concentrations of the 11 herbicides and 2 metabolites determined by GC/MS,
Table 1. Summary of herbicide concentrations detected in pre-planting, post-planting, and harvest samples, 1989 [μg/L, micrograms per liter. Concentrations were determined by gas chromatography/mass spectrometry with detection limits of 0.05 μg/L for all herbicides except cyanazine, which is 0.20 μg/L]

<table>
<thead>
<tr>
<th>Herbicide</th>
<th>Number of samples</th>
<th>Pre-Planting</th>
<th>Post-Planting</th>
<th>Harvest Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Detections (percent)</td>
<td>Median (μg/L)</td>
<td>Maximum (μg/L)</td>
</tr>
<tr>
<td>Alachlor</td>
<td>55</td>
<td>18</td>
<td>&lt;0.05</td>
<td>0.44</td>
</tr>
<tr>
<td>Atrazine</td>
<td>55</td>
<td>91</td>
<td>0.23</td>
<td>1.70</td>
</tr>
<tr>
<td>Deethyl-atrazine</td>
<td>55</td>
<td>54</td>
<td>0.05</td>
<td>0.39</td>
</tr>
<tr>
<td>Deisopropyl-atrazine</td>
<td>55</td>
<td>9</td>
<td>&lt;0.05</td>
<td>0.59</td>
</tr>
<tr>
<td>Cyanazine</td>
<td>55</td>
<td>5</td>
<td>&lt;0.20</td>
<td>0.52</td>
</tr>
<tr>
<td>Metolachlor</td>
<td>55</td>
<td>34</td>
<td>&lt;0.05</td>
<td>0.53</td>
</tr>
<tr>
<td>Metribuzin</td>
<td>55</td>
<td>2</td>
<td>&lt;0.05</td>
<td>0.16</td>
</tr>
<tr>
<td>Propazine</td>
<td>55</td>
<td>0</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>Prometon</td>
<td>55</td>
<td>0</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>Simazine</td>
<td>55</td>
<td>7</td>
<td>&lt;0.05</td>
<td>8.70</td>
</tr>
</tbody>
</table>

was calculated for each sample. The results (fig. 2C) show that the median concentration of total herbicides in the 1989 post-planting samples was 8.7 μg/L, or more than 20 times larger than the pre-planting concentrations. Furthermore, resampling studies in one-third of the basins during 1990 verified these concentrations (fig. 2C).

The apparent order of decreasing stability of the herbicides and metabolites on the basis of results shown in figure 2 and listed in table 1 is atrazine, deethylatrazine, metolachlor, cyanazine, deisopropylatrazine, and alachlor. This stability relation may be interpreted from the number of detections of herbicides in both the pre-planting and post-harvest samples and in the range of the concentrations during those two sampling periods (figs. 2A and 2B). Decomposition rates in soil from the published literature support these findings (Nash, 1988). For example, atrazine has a reported half-life of 140 days; metolachlor, 90 days; cyanazine, 85 days; and alachlor, 50 days. Half-lives were not known for deethylatrazine and deisopropylatrazine, but it is known that deethylatrazine will remain in the soil from 1 year to the next (Mills, 1991; Mills and Thurman, 1994).

The temporal trends in the number of detections of various herbicides are significant for several reasons. First, trends indicate that some of the compounds persist from year to year in soil and water. Second, degradation products, such as deethylatrazine, are both persistent and mobile in water. Third, the data suggest that the DAR, which has been proposed as an indicator of nonpoint-source contamination of ground water (Thurman and others, 1994), might also be used as a tracer of ground-water discharge into rivers.
Figure 2. Box plots of (A) herbicides detected during three sampling periods; (B) streamflow, deethylatrazine, and deethylatrazine-to-atrazine ratio; and (C) total herbicide concentrations in 1989 and 1990 for pre-planting and post-planting periods.
Degradation of Triazine Herbicides

The degradation pathway for the dealkylation reactions of major triazine herbicides to deisopropylatrazine and to deethylatrazine is shown in figure 3. The triazine herbicides atrazine, cyanazine, simazine, and terbuthylazine may degrade to the same metabolite, deisopropylatrazine. By similar fashion, atrazine and propazine may degrade to deethylatrazine. Field studies (Mills, 1991; Mills and Thurman, 1994) show that atrazine degrades to both deethylatrazine and deisopropylatrazine at relatively constant rates, resulting in a $D^2R$ of approximately 0.40 (Thurman and others, 1994). Mills and Thurman (1994) showed that there is preferential loss of deisopropylatrazine with depth because of the ease of removing an ethyl group over an isopropyl group. Thus, deethylatrazine will be transported downward in soil and eventually will be detected in ground water, whereas $D^2R$ is much smaller in ground water than in surface water. Thus, these two compounds may be used to follow rate of flow of herbicides through the unsaturated zone. Slow transport through the unsaturated zone would remove deisopropylatrazine but not deethylatrazine. Rapid transport (macropore flow) would result in the presence of both metabolites. Also, the $D^2R$ may be used to indicate
surface-water flow because of the relatively constant ratio of the metabolites in surface water. This result suggests that degradation of both metabolites is slow in surface water, a result born out in studies by Pereira and Rostad (1990) on the Mississippi River.

Adams and Thurman (1991) found that atrazine transport through the unsaturated zone produced a DAR greater than 1.0, whereas the DAR for atrazine transported from the field in surface runoff was much less than 1.0. Furthermore, deisopropylatrazine degraded rapidly in the unsaturated zone but was an important metabolite in surface runoff from fields (Mills, 1991; Mills and Thurman, 1994). Thus, the DAR may be indicative of ground-water recharge by atrazine-laden water. For example, the median DAR was 0.30 in the pre-planting samples, less than 0.10 in the post-planting samples, and 0.4 in the harvest samples (fig. 2B). It is hypothesized that the large decrease in the DAR from 0.3 to less than 0.10 indicates that runoff of recently applied herbicides contains a small ratio of degradation product, in spite of the increased detections and greater concentrations of deethylatrazine (fig. 2B). The large increase in the DAR from less than 0.10 to 0.40 in the post-planting to the harvest samples may reflect the discharge of alluvial ground water that provides stream base flow and the flux of herbicides into surface water.

Contamination of Alluvial Aquifers

A process for surface-water contamination of alluvial ground water is shown in figure 4. The pre-planting samples had a large DAR (0.30), but they also contained a few detections of deisopropylatrazine (9 percent). These results suggest both a surface- and ground-water origin of herbicides during this sampling period as do the discharge records. The surface component likely is due to recent spring melting of snow and ice. The post-planting samples collected during a period of runoff had a small DAR (less than 0.10) and the greatest number of detections of deisopropylatrazine (54 percent), which indicates that surface runoff is the major contributor of herbicides at this time. Finally, the post-harvest sampling during a low streamflow period had the largest DAR (0.40) and no detections of deisopropylatrazine, which indicates that alluvial ground water was likely the major source of herbicide at that time (Squillace and Thurman, 1992). Measurements of streamflow (fig. 4) indicate that base-flow conditions predominated during the harvest sampling.

Surface water contaminated during the spring runoff is hypothesized to contribute significantly to the contamination of alluvial ground water. Mechanisms include a rapid increase in stream stage that occurs in spring when rivers are bankfull. During this time, ground-water gradients may reverse and cause streamwater to flow into adjacent alluvial aquifers (fig. 4). Contaminated surface water also may enter alluvial aquifers by recharge from floodwaters and runoff from areas that discharge onto the alluvial plain. Later, this discharge becomes a recharge for the alluvial aquifer.
Furthermore, large alluvial plains typically are planted to row crops in the “Corn Belt,” where herbicides are applied directly to the alluvial soils with the potential for leaching to the shallow ground water. Studies of metabolite degradation continue to improve the understanding of these various transport processes.

REFERENCES CITED


The Transport and Degradation of Cyanazine Metabolites in Surface Water of the Midwestern United States

By M.T. Meyer and E.M. Thurman

Abstract

Cyanazine was detected in 73 percent, cyanazine amide in 65 percent, deethylycyanazine in 36 percent, and deisopropylatrazine in 52 percent of the samples collected during the first storm runoff after herbicide application in a reconnaissance study of stream water from 122 basins in a 10-State area in the Midwestern United States in 1989. Furthermore, these compounds were detected in as many as 30 percent of the samples collected in the spring before planting and in the fall of the year during low streamflow. Analysis of samples collected from several stream sites during storm-runoff throughout the spring and early summer of 1990 indicate that cyanazine degrades to deisopropylatrazine and that the deisopropylatrazine-to-deethylatrazine ratio (D2R) is an indicator of the amount of cyanazine relative to atrazine that is used in the basin.

INTRODUCTION

Contamination of surface and ground water by chemicals applied for agricultural usage is a significant problem in the midcontinent region (Humenik and others, 1987). Pre-emergent herbicides used for weed control comprise a substantial amount of this agricultural usage. Studies have shown that in the Midwestern United States herbicide contamination of surface water is a periodic and persistent problem (Spalding and Snow, 1989; Stamer and others, 1990; Goolsby and others, 1991) and now there is concern that herbicide metabolites also may be a potential contamination problem in surface water. Most herbicide transport in surface water occurs in the spring and early summer (Thurman and others, 1991; Squillace and Thurman, 1992). Also, it has been demonstrated that the effect of the spring flush on herbicide concentration in surface water is a regional phenomenon in the Midwestern United States (Goolsby and others, 1989; Thurman and others, 1991, 1992).

Recent studies show that herbicide metabolites can be useful in determining transport and contamination processes (Adams and Thurman, 1990; Thurman and others, 1991, 1992). Thurman and others (1991, 1992) proposed that the ratio of deethylatrazine, a metabolite of atrazine, to atrazine is an indicator of alluvial ground-water contributions to surface water and that the more rapidly degraded metabolite of atrazine, deisopropylatrazine, can be an indicator of surface-water runoff. Thus, the presence of deisopropylatrazine in ground water, along with a low deethylatrazine-to-atrazine ratio (DAR), may indicate the interaction of surface water with ground water.

The potential for using herbicide metabolites as indicators of transport processes is a relatively new concept that might be extended to the other major herbicides found in surface water, such as cyanazine, alachlor, and metolachlor. Cyanazine, one of the most widely used herbicides in the Midwest, readily metabolizes to form a suite of compounds that could be used as indicators. However, little is known about the occurrence of cyanazine metabolites in surface water. The objectives of this paper are to (1) describe the occurrence of cyanazine metabolites in surface water, (2) present evidence that cyanazine degrades to deisopropylatrazine, and (3) demonstrate that cyanazine and metabolite ratios are indicators of transport. To accomplish these objectives, this paper presents the results from a herbicide reconnaissance study of stream water in the Midwestern United States conducted in 1989 and from a storm-runoff sampling study of stream water conducted in 1990.
STUDY DESIGN AND METHODS OF ANALYSIS

The design of the herbicide-reconnaissance study of stream water in the Midwest has been described in Goolsby and others (1989) and Thurman and others (1992). Briefly, 149 sampling sites in 122 river basins throughout a 10-State area were selected using a stratified random-sampling procedure. Each site was sampled in the spring before the application of herbicides, after application of herbicides during the first storm runoff, and in the fall during a period of low flow.

The storm-runoff study, conducted in 1990, was designed to assess the effects of successive storms on the concentration of herbicides in stream water from spring through early to midsummer. For this study, automated water samplers were installed at nine stream sites in five States (Illinois, Iowa, Kansas, Nebraska, and Ohio). The auto-samplers were programmed to collect samples every 1 to 2 days during low flow and every 1 to 2 hours during periods of storm runoff. Approximately 20 percent of the samples collected from each site were analyzed for herbicides by gas chromatography/mass spectrometry (GC/MS).

Samples were analyzed for triazine herbicides using solid-phase extraction, GC/MS after the methods of Thurman and others (1990) and Meyer and others (1993). GC/MS analyses for the cyanazine metabolites, deethylcyanazine and cyanazine amide, were performed by GC/MS using a capillary GC column with a 5-percent phenyl phase. The quantitation limit for cyanazine, cyanazine amide, and deisopropylatrazine was 0.05 µg/L, and for deethylcyanazine amide, 0.2 µg/L.

RESULTS AND DISCUSSION

Reconnaissance Study Variation by Sampling Round

Samples from the herbicide reconnaissance study in 1989 were analyzed to determine the occurrence of cyanazine metabolites in stream water in the Midwestern United States. In the first round, samples were collected from mid-March through mid-April, before herbicides had been applied. Cyanazine was detected in 14 percent, cyanazine amide in 20 percent, and deethylcyanazine in 9 percent of the samples (table 1). The data from this sample round suggest that cyanazine metabolites can be available for transport into surface water throughout the year.

Table 1. Summary of surface-water herbicide reconnaissance data for cyanazine and cyanazine metabolites, 1989

<table>
<thead>
<tr>
<th>Sample round</th>
<th>Compound</th>
<th>Cyanazine</th>
<th>Cyanazine amide</th>
<th>Deethylcyanazine</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Quantitation limit (µg/L)</td>
<td>0.05</td>
<td>0.05</td>
<td>0.20</td>
</tr>
<tr>
<td>1</td>
<td>Percent detections</td>
<td>17</td>
<td>17</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Number of analyses</td>
<td>57</td>
<td>54</td>
<td>54</td>
</tr>
<tr>
<td></td>
<td>Average (µg/L)</td>
<td>0.24</td>
<td>0.13</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td>Standard deviation (µg/L)</td>
<td>0.14</td>
<td>0.06</td>
<td>&lt;0.20</td>
</tr>
<tr>
<td></td>
<td>Range (µg/L)</td>
<td>0.10-0.60</td>
<td>0.08-0.20</td>
<td>&lt;0.20</td>
</tr>
<tr>
<td>2</td>
<td>Percent detections</td>
<td>73</td>
<td>65</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td>Number of analyses</td>
<td>142</td>
<td>105</td>
<td>105</td>
</tr>
<tr>
<td></td>
<td>Average (µg/L)</td>
<td>7.1</td>
<td>1.6</td>
<td>0.72</td>
</tr>
<tr>
<td></td>
<td>Standard deviation (µg/L)</td>
<td>1.1</td>
<td>2.1</td>
<td>&lt;0.20</td>
</tr>
<tr>
<td></td>
<td>Range (µg/L)</td>
<td>0.05-6.1</td>
<td>0.09-11.1</td>
<td>0.05-2.5</td>
</tr>
<tr>
<td>3</td>
<td>Percent detections</td>
<td>29</td>
<td>34</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Number of analyses</td>
<td>142</td>
<td>139</td>
<td>139</td>
</tr>
<tr>
<td></td>
<td>Average (µg/L)</td>
<td>0.15</td>
<td>0.11</td>
<td>&lt;0.20</td>
</tr>
<tr>
<td></td>
<td>Standard deviation (µg/L)</td>
<td>0.10</td>
<td>0.07</td>
<td>&lt;0.20</td>
</tr>
<tr>
<td></td>
<td>Range (µg/L)</td>
<td>0.07-0.45</td>
<td>0.05-0.38</td>
<td>&lt;0.20</td>
</tr>
</tbody>
</table>

1 Average concentration based only on samples for which the compound exceeded the quantitation limit.
The samples for round 2 were collected during the first large storm runoff occurring in each basin after the majority of herbicides had been applied to the fields. Round-2 samples were collected between mid-May and mid-August. In this sample round, cyanazine was detected in 73 percent, cyanazine amide in 65 percent, and deethylcyanazine in 36 percent of the samples (table 1). These data show that cyanazine metabolites are readily generated in the soil and transported into surface water shortly after herbicide application. The average concentration (calculated only for compounds that were detected at quantifiable concentrations) for the round-2 samples was 7.1 ug/L for cyanazine, 1.6 ug/L for cyanazine amide, and 0.72 ug/L for deethylcyanazine (table 1). The U.S. Environmental Protection Agency (USEPA) Health Advisory Level (HAL) for cyanazine is 1.0 ug/L (U.S. Environmental Protection Agency, 1992).

Round-3 samples were collected from late September through late-November. The stream sites were sampled during low flow when most of the stream water could be attributed to ground-water discharge. In this round, cyanazine was detected in 29 percent, cyanazine amide in 34 percent, and deethylcyanazine in 0 percent of the samples. The results from this round are consistent with the round 1 data in that some cyanazine and cyanazine amide persisted and was still detectable in many streams. Because the samples from round 3 were collected during low flow, the occurrence of cyanazine and cyanazine amide most likely represents ground water contributions to stream water; whereas samples collected in round 1 were not necessarily collected during low-flow conditions. Therefore, the presence of cyanazine and cyanazine amide in round-1 samples could reflect either overland-flow runoff or ground water contributions to stream water. The average concentration of each compound for the first and third rounds was much smaller than it was for the round-2 samples. For example, the average concentration for cyanazine was 0.24 and 0.15 µg/L; cyanazine amide, 0.13 and 0.11 µg/L; and deethylcyanazine 0.2 less than 0.20 µg/L for rounds 1 and 3, respectively (table 1).

Deisopropylatrazine: A Degradation Product of Cyanazine

Deethylatrazine and deisopropylatrazine are important, but not exclusive, degradation products of atrazine. For example, propazine and simazine degrade to deethylatrazine and deisopropylatrazine, respectively; however, about 15 to 20 times more atrazine than simazine or propazine is applied in the United States (Gianessi and Puffer, 1991). Therefore, the presence of deisopropylatrazine and deethylatrazine in surface water and ground water is ascribed almost exclusively to the degradation of atrazine. However, there is evidence that cyanazine also degrades to deisopropylatrazine. Sirons and others (1973) noticed that, when cyanazine was applied to field plots to which atrazine previously had been applied, the concentration of deisopropylatrazine increased. Also, a study by Benyon and others (1972) indicates that cyanazine degrades to deisopropylatrazine. This is important because atrazine use is only three times that of cyanazine in the United States (Gianessi and Puffer, 1991). Therefore, in areas where cyanazine is used in approximately the same quantities as atrazine, a substantial amount of the deisopropylatrazine produced and transported into surface water might be from the degradation of cyanazine.

Field-dissipation studies of atrazine have shown that the deisopropylatrazine-to-deethylatrazine ratio (D²R) is about 0.3 to 0.5 (E. M. Thurman, U.S. Geological Survey, written commun., 1993). The D²R obtained from surface-water samples where atrazine is the primary triazine herbicide are in good agreement with the atrazine field-dissipation studies (that is, the D²R generally ranges from 0.3 to 0.5). However, in surface-water samples where the concentration of cyanazine is about the same concentration as that of atrazine, the D²R increases from 0.7 to larger than 1.0.

This point can be illustrated by examining data from water samples collected from a basin where much more atrazine was applied than cyanazine, and in another basin where approximately the same amounts of atrazine and cyanazine were applied. For example, figures 1A and 1B shows that water samples collected from the Delaware River storm-runoff site had much larger concentrations of atrazine than cyanazine under low-flow and high-flow conditions. The average concentration for atrazine was 8.9 µg/L and for cyanazine was 0.29 µg/L. In contrast to the Delaware River, samples from the Iroquois River storm-runoff site (fig. 1D) had cyanazine concentrations that were mostly equal to or less than five times the concentration of atrazine. For example, the average concentration for atrazine was 2.6 µg/L and for cyanazine was 1.7 µg/L for samples collected from the Iroquois River storm-runoff site. Numerous samples from both the Delaware and Iroquois River sampling sites exceeded the USEPA...
Figure 1. Streamflow and concentrations of atrazine and cyanazine in samples from the Delaware River are shown in graphs A and B, respectively, and for the Iroquois River in C and D, respectively, from April-September 1990. MCL = maximum contaminant level for atrazine and HAL = Health Advisory Level for cyanazine (U.S. Environmental Protection Agency, 1992). Minor tick marks are in weeks. General trend lines in graphs B and D are not regressed.
Maximum Contaminant Level (MCL) for atrazine of 3.0 µg/L (U.S. Environmental Protection Agency, 1992) except during low flow (figs. 1A and 1C). However, only one sample from the Delaware River exceeded the HAL of 1.0 µg/L for cyanazine, whereas the concentration of cyanazine exceeded the HAL in 19 samples from the Iroquois River.

Figure 1D also shows that the concentrations of atrazine and cyanazine in water from the Iroquois River storm-runoff site decreased in a fairly linear fashion from mid-June through August. Furthermore, the concentration of cyanazine appears to have decreased more rapidly than the concentration of atrazine. This is consistent with observations in the literature that cyanazine degrades more rapidly than atrazine. The systematic decrease in the concentration of herbicides indicates that 4 to 5 weeks after herbicide application the amount of herbicide available for transport from the field into surface water diminishes rapidly. Therefore, the production of metabolites by cyanazine relative to atrazine should decrease as a function of time after herbicide application. The evidence presented here indicates that one of the degradation products of cyanazine is deisopropylatrazine; field studies are underway to confirm this hypothesis.

Cyanazine Ratios as Transport Indicators

To look at the relation between the amount of cyanazine relative to atrazine and its effect on the production of deisopropylatrazine, it is instructive to examine the atrazine-to-cyanazine ratio (ACR) and the D^2R. Figure 2A shows that the ACR in samples collected from the Delaware River was much larger than 5. For these same samples, figure 2B shows that the D^2R for most of the samples was less than 0.50 and, except for one sample, all had a D^2R of less than 0.55. Furthermore, the average D^2R for these samples was 0.44. The variation of the D^2R in the samples from the Delaware River are in good agreement with the results from field-dissipation studies of atrazine (E.M. Thurman, U.S. Geological Survey, oral commun., 1993). Therefore, the D^2R indicates that atrazine is the primary source of the deethylatrazine and deisopropylatrazine that were transported into the Delaware River. This is further supported by the fact that the concentrations of simazine and propazine were much less than that of cyanazine for the samples collected from this storm-runoff sampling site.

In contrast, in the Iroquois River Basin contains approximately equal amounts of atrazine and cyanazine are applied (fig. 3A), and the D^2R is elevated (fig. 3B) from less than 0.5 to between 0.7 and 1.1 shortly after the application of herbicides. Furthermore, for the first 1.5 months after application when the majority of cyanazine, transport occurred (fig. 10), most ACR's were less than 2.0. The ACR shows a steady increase from mid-May through August (fig. 3A), indicating that cyanazine degrades more rapidly than atrazine in soil, as reflected in changing concentrations of atrazine and cyanazine in water samples from successive storm-runoff events (fig. 1D). Thus, the decreasing availability of cyanazine for transport into surface water relative to atrazine was reflected by the increasing ACR in the surface-water samples with time.

Figure 3B shows that the D^2R of most of the samples from the Iroquois River were larger than 0.50. During the first 1.5 months after herbicide application when the ACR of most of the samples was less than 2.0, the D^2R of most of the samples was larger than 0.70. The high D^2R in these samples indicates that cyanazine was responsible for at approximately one-third of the deisopropylatrazine transported into the Iroquois River during this time. From July through August (fig. 3B) there was a marked decrease in the D^2R, which correlated with an increase in the ACR. These data suggest that cyanazine is a major source of deisopropylatrazine in the Iroquois River and that, as the concentration of cyanazine relative to atrazine decreases, the D^2R decreases because atrazine then becomes the primary source of deisopropylatrazine.

The data from the Delaware and Iroquois Rivers shows that the D^2R can be used as an indicator of transport of other herbicides, such as cyanazine or simazine and propazine. Furthermore, the D^2R could be used as an indication that further analyses are needed, such as analyses for the polar metabolites of cyanazine.

CONCLUSIONS

Data from the herbicide reconnaissance study show that cyanazine amide and deethylcyanazine are important degradation products of cyanazine and are readily transported into surface water. Furthermore, cyanazine and cyanazine amide were detected in water samples from the pre-herbicide application and fall sampling periods of the reconnaissance study.
Figure 2. Discrimination graphs of (A) atrazine-to-cyanazine ratios (ACR) and (B) deisopropylatrazine-to-deethylatrazine ratios ($D^2R$), in water samples from the Delaware River, April-September 1990. For (B), the $D^2R$ graph, black squares correspond to when the ACR was greater than 5; for the unfilled triangles, there was no corresponding ACR. Minor tick marks are in weeks.

This demonstrates that cyanazine and cyanazine amide can be available for transport into surface water long after herbicides have been applied. Data from the Delaware River in Kansas show that the $D^2R$ in surface water from basins where much more atrazine than cyanazine is applied is similar to the $D^2R$ from atrazine field-dissipation studies. However, for basins where atrazine and cyanazine are applied in approximately equal amounts, such as the Iroquois River Basin in Illinois, the $D^2R$ is considerably larger. Data from the Iroquois River showed that, when ACR is less than 2, atrazine was responsible for at least one-third of the deisopropylatrazine transported into the river. The increased contribution of deisopropylatrazine by
cyanazine was reflected by an increase in the $D^2R$ to values larger than 0.70. Furthermore, the samples from the Iroquois River show that, as the amount of cyanazine relative to atrazine decreases with time, atrazine becomes the primary source of deisopropylatrazine, which is reflected by a decrease in the $D^2R$. The data from these two storm-runoff sites indicate that cyanazine degrades to deisopropylatrazine. Finally, the $D^2R$ is a sensitive indicator of whether the degradation of herbicides other than atrazine contributes a significant amount of the deisopropylatrazine that is transported into surface water.
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By G.P. Johnson and R.H. Coupe

Abstract

The Sangamon River, located in east-central Illinois, drains some of the most intensively used agricultural land in the Midwest. Effects of agricultural practices in the drainage basin on stream-water quality were investigated by collecting surface-water samples from April 1991 through March 1992 at Monticello, Illinois. Samples were analyzed for concentrations of selected herbicides and nitrate. Total load was calculated and compared to estimated application totals of each compound in the drainage basin above Monticello.

During the study period, 1,607 pounds of atrazine were transported by the river; this mass represents 1.4 percent of the total annual application of 113,700 pounds. The river transported 669 pounds of cyanazine—a mass equal to 1.6 percent of the total annual application of 41,900 pounds. About 353 pounds of alachlor were transported by the river (0.31 percent of the 112,300 pounds applied). About 12,100 tons of nitrogen fertilizer were applied, and 3,393 tons of nitrate as nitrogen were transported by the river (28 percent of the total amount applied). However, other natural and human-derived sources of nitrate could have contributed to this total load.

The timing of chemical application and the quantity of rainfall and runoff after herbicide application affected the concentrations. Herbicide concentrations were highest in early spring during storms immediately following application. Peak concentrations for atrazine, cyanazine, and alachlor occurred in May; these concentrations were 21, 16, and 8.8 micrograms per liter, respectively. Nitrate concentrations were at or above the U.S. Environmental Protection Agency’s maximum contaminant level of 10 milligrams per liter from the beginning of the study until June 11, 1991. Nitrate concentrations then remained less than the maximum contaminant level until November 1991.

INTRODUCTION

Stream-water-quality criteria for agricultural chemicals are expressed in terms of chemical concentrations. Concentrations of these chemicals in streams provide an indicator of whether the water quality is suitable for the designated uses of the stream. Agricultural-chemical concentrations, especially in small streams, are affected by the timing, intensity, and duration of rainfall, which can vary from year to year. Therefore, the effect of agricultural practices on stream-water quality cannot be assessed directly from concentration data. The effects of agricultural practices on stream-water quality can be better understood by measuring the transport of agricultural chemicals in streams. If the amounts of these chemicals applied within a drainage basin are known, annual losses of these chemicals from agricultural fields into a stream can be determined.

Agricultural chemicals applied to croplands can undergo physical, chemical, and biological transformations. Depending on the properties of a chemical and on conditions such as rainfall, wind, soil moisture, soil type, and temperature, a chemical can sorb to soil

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particles, be transported through the soil column, undergo biological or chemical transformations, and (or) volatilize to the atmosphere (Biggar and Seiber, 1987). Transport of these chemicals into rivers can be caused by storm runoff from cropland, tributary flow, ground-water discharge, and (or) atmospheric deposition.

Atrazine and alachlor are the most heavily used agricultural chemicals in Illinois and in the United States. Atrazine and cyanazine are preemergent and postemergent herbicides used on corn, and alachlor is a preemergent herbicide used on corn and soybeans (Pike and others, 1990). Application of these chemicals usually is accomplished by surface spraying in the spring prior to planting.

Nitrogen fertilizer is applied to croplands as either anhydrous ammonia, urea, ammonium nitrate, or as a nitrogen solution (University of Illinois Cooperative Extension Service, 1990). Most of the nitrogen is applied by injection of anhydrous ammonia into the soil in March and April before planting. Nitrogen also can be applied in late fall and early winter in any of the different forms.

The Sangamon River is located in east-central Illinois and has a drainage area of 550 square miles at Monticello, Ill. (fig. 1). The land use of the basin above Monticello is predominantly row-crop agriculture--mostly corn and soybeans. No major communities are upstream from Monticello. The Sangamon River Basin above Monticello lies in the Bloomington Ridged Plain, which is characterized by low, broad ridges separated by wide, gently undulating moraines and wooded areas in the river valleys (Leighton and others, 1948).

The purpose of this paper is to describe the total load and concentrations of selected herbicides and nitrate in the Sangamon River. To measure the transport of agricultural chemicals in the Sangamon River in east-central Illinois, surface-water samples were collected from the Sangamon River at Monticello from April 12, 1991, through March 25, 1992, and were analyzed for concentrations of dissolved atrazine, dissolved cyanazine, dissolved alachlor, and nitrate. Total annual loads were calculated for each compound and compared with application amounts. These annual loads were compared to loads calculated from an earlier study of the same basin. Water discharges were determined from records collected at a streamflow-gaging station at the sampling site.

METHODS

An automatic sampler was installed in the streamflow-gage house on the Sangamon River at Monticello to collect surface-water samples. The automatic sampler was programmed to collect water samples at a frequency associated with a given water-level (stage) in the stream or a rate-of-change in stage. At base flow, samples were collected once every 48 hours. During high flow, samples were collected three times per day. Sample collection was increased up to four times daily with a rapid rise in stage.

Water samples were pumped through Teflon tubing into clean 350-mL glass bottles. Samples were picked up at least twice weekly and more often during high-flow periods. The bottles were capped with aluminum foil and transported to the U.S. Geological Survey (USGS) office in Urbana, Ill., for processing. Water samples analyzed for herbicide concentrations were filtered through a glass-fiber filter and shipped on ice to the USGS office in Lawrence, Kan. The herbicide samples were analyzed using solid-phase extraction with Gas Chromatography/Mass Spectrometry (GC/MS) as described in Goolsby and others (1991). Water samples for nitrate were filtered through a 0.45-micron pore-size filter, preserved with mercuric
chloride (HgCl₂), and then shipped to the USGS National Water Quality Laboratory (NWQL) in Arvada, Colo., for analyses.

After October 1991, the automatic sampler was removed because of the potential of samples freezing and the samples were collected manually. Because herbicide detections are less frequent, and concentrations are much lower in the fall and winter when compared to spring and summer (Thurman and others, 1991), sampling frequency was approximately twice monthly from October 1991 through March 1992.

Daily mass transport of the selected herbicides and nitrates were calculated from concentration and streamflow data. For each compound, a graph showing the instantaneous concentration as a function of time was plotted. Adjacent points on these graphs were connected by straight lines, and this trace was digitized. A linear-interpolation algorithm was then used to estimate concentrations at 4-hour intervals. Discharge data, which were available at 15-minute intervals, were averaged to estimate the mean discharge for the 4-hour period. This mean discharge was multiplied by the concentration and a unit conversion factor that estimated the mass transport rate for that 4-hour period. These rates were multiplied by the duration of the period to estimate the load (total mass transported), and the loads were summed to estimate the total load for each month.

RESULTS

The monthly mass transports of atrazine and nitrate as nitrogen during the study period are shown in figure 2. The monthly mean streamflow for October 1990 through March 1992 and the historical monthly mean streamflow also are shown. Large amounts of atrazine and nitrate were transported by the Sangamon River at Monticello at the beginning of the study. Transport rates during April 1991 were 166 pounds per month of atrazine and 547 tons per month of nitrate as nitrogen. In May 1991, transport rates increased and peaked at 1,211 pounds of atrazine and 891 tons of nitrate per month. Transport rates for all compounds analyzed were largest in May 1991 and were smallest in September 1991 during an extended dry period. Nitrate transport rates and streamflow increased beginning in November 1991. Atrazine transport rates also increased as streamflow increased in November, but the increase was small compared to the transport rates for April, May, and June 1991.

Table 1 lists the masses of atrazine, cyanazine, alachlor, and nitrate as nitrogen transported by month. The largest monthly transport rates for atrazine, cyana-
Table 1. Mass transport of agricultural chemicals in the Sangamon River at Monticello, Ill., April 1991-March 1992 and April-August 1990

(Q, water discharge; ft³/s, cubic feet per second; lbs, pounds; NO2 + NO3, nitrite+nitrate; -, not applicable)

<table>
<thead>
<tr>
<th>Month</th>
<th>Mean daily Q (ft³/s)</th>
<th>Atrazine (lbs)</th>
<th>Cyanazine (lbs)</th>
<th>Alachlor (lbs)</th>
<th>Nitrate (tons)</th>
<th>Mean daily Q (ft³/s)</th>
<th>Atrazine (lbs)</th>
<th>Cyanazine (lbs)</th>
<th>Alachlor (lbs)</th>
<th>Nitrate (tons)</th>
</tr>
</thead>
<tbody>
<tr>
<td>April 1991-March 1992</td>
<td>710</td>
<td>166</td>
<td>64</td>
<td>54</td>
<td>547</td>
<td>411</td>
<td>68</td>
<td>327</td>
<td>1,489</td>
<td></td>
</tr>
<tr>
<td>April 1991-March 1992</td>
<td>940</td>
<td>1,211</td>
<td>558</td>
<td>268</td>
<td>891</td>
<td>1,524</td>
<td>797</td>
<td>1,480</td>
<td></td>
<td></td>
</tr>
<tr>
<td>June</td>
<td>242</td>
<td>148</td>
<td>23</td>
<td>18</td>
<td>193</td>
<td>1,744</td>
<td>1,155</td>
<td>1,415</td>
<td></td>
<td></td>
</tr>
<tr>
<td>July</td>
<td>33</td>
<td>4.4</td>
<td>35</td>
<td>.43</td>
<td>3.7</td>
<td>887</td>
<td>227</td>
<td>764</td>
<td></td>
<td></td>
</tr>
<tr>
<td>August</td>
<td>16</td>
<td>.64</td>
<td>.07</td>
<td>.08</td>
<td>.22</td>
<td>120</td>
<td>8.5</td>
<td>46</td>
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<td>September</td>
<td>4.0</td>
<td>.15</td>
<td>.04</td>
<td>.08</td>
<td>.15</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>October</td>
<td>40</td>
<td>3.3</td>
<td>.10</td>
<td>.80</td>
<td>4.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>November</td>
<td>250</td>
<td>20</td>
<td>.31</td>
<td>2.1</td>
<td>139</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>December</td>
<td>545</td>
<td>23</td>
<td>.18</td>
<td>3.6</td>
<td>608</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>January</td>
<td>240</td>
<td>6.4</td>
<td>.43</td>
<td>.26</td>
<td>227</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>February</td>
<td>360</td>
<td>14</td>
<td>.27</td>
<td>1.3</td>
<td>377</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>March</td>
<td>370</td>
<td>9.1</td>
<td>.07</td>
<td>2.5</td>
<td>403</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TOTAL</td>
<td>1,407</td>
<td>669</td>
<td>353</td>
<td>3,393</td>
<td></td>
<td>2,256</td>
<td>4,048</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Atrazine, and alachlor were in May 1991, representing 75, 83 and 81 percent, respectively, of the total mass transport during the study period. The largest nitrate transport rate also was in May 1991, but the mass transported represented only 26 percent of the total mass of nitrate transported during the entire period. Mass transport of nitrite plus nitrate as nitrogen (NO₂ + NO₃) and atrazine determined in a previous study at the same station (Coupe and Johnson, 1991) during the period April through August 1990 also is shown in table 1. The previous study was similar to this one, except that samples were analyzed for NO₂ + NO₃ instead of only nitrate and most of the atrazine concentrations were determined by an immunoassay method (Thurman and others, 1991). Only a few samples were analyzed by GC/MS to determine the concentration of atrazine.

Ambient stream-water-quality data show that the contribution of nitrite to the NO₂ + NO₃ concentration in the Sangamon River usually is very small—less than 1 percent (Richards and others, 1992). Therefore, the mass of NO₂ + NO₃ transported in 1990 can be compared with the nitrate transport computed for 1991. The results of the immunoassay analysis provide a good indication of the atrazine concentration and were used to estimate the atrazine concentrations when values determined by GC/MS were not available. The mass transport for the 1990 study was estimated using the same method as the 1991-92 study.

Most of the atrazine for the study period was transported between the beginning of April 1991 and the end of August 1991 (table 1). More than 95 percent of the total atrazine load transported by the river at Monticello between April 1991 and March 1992 was transported during April through August 1991. Thus, the data presented in table 1 for the 1990 study probably represent an estimate of most of the total atrazine load for that year.

The total mass of NO₂ + NO₃ and atrazine transported during the 5-month study in 1990 exceeded that for nitrate and atrazine transported during the entire 12-month 1991-92 study. This could be because of the high streamflows during the 1990 study. In the spring of 1990, the largest monthly mass transport for atrazine was in June; in the spring of 1991, the largest monthly mass transport of atrazine was in May. The monthly mean discharge for June 1990 was 1,744 ft³/s; for June 1991, it was 242 ft³/s. Nitrate load at this site was dependent on streamflow. Regardless of season, an increase in streamflow was accompanied by an increase in nitrate mass transport. A plot of monthly mean discharge against monthly nitrate mass transport for data from all 12 months of the study plus data from the 5-month previous study is shown in figure 3.

The total mass transport of selected herbicides and nitrate in the Sangamon River at Monticello, as well as the total amount of these compounds applied in the drainage basin and the percentage transported in the Sangamon River, are shown in table 2. Nitrogen-application rates were obtained from the U.S. Environmental Protection Agency (USEPA) (1990) and estimated herbicide application rates were obtained from Gianessi and Puffer (1991). The mass transport of nitrate is shown for reference as a percentage of the
Figure 3. Monthly mean discharge and nitrate as nitrogen load, Sangamon River at Monticello, Illinois, April–August 1990.


<table>
<thead>
<tr>
<th>Compound</th>
<th>April 1991–March 1992</th>
<th>April–August 1990</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Annual application</td>
<td>Total load</td>
</tr>
<tr>
<td>Atrazine</td>
<td>113,700 lbs</td>
<td>1,607 lbs</td>
</tr>
<tr>
<td>Cyanazine</td>
<td>41,900 lbs</td>
<td>669 lbs</td>
</tr>
<tr>
<td>Alachlor</td>
<td>112,300 lbs</td>
<td>353 lbs</td>
</tr>
<tr>
<td>Nitrate</td>
<td>12,100 tons</td>
<td>3,393 tons</td>
</tr>
</tbody>
</table>

Source: Gianessi and Puffer, 1990

amount applied even though other sources of nitrate, both natural and human derived, can contribute to the mass transported.

Atrazine transported in the Sangamon River for the 1990 and the 1991-92 studies was 2.0 and 1.4 percent, respectively, of the amount applied. Wauchope (1978) indicates that losses up to 5 percent can be expected for herbicides, depending on the slope of the land and the timing of rainfall following their application. The Sangamon River is a secondary tributary to the Mississippi River. Goolsby and others (1991) calculated that 0.9 percent of the applied atrazine in the Mississippi River Basin flowed into the Gulf of Mexico. Although cyanazine was applied in smaller amounts than was atrazine or alachlor, more cyanazine was transported than the other two herbicides. The amount of alachlor transported was small compared with the amounts of atrazine and cyanazine.

The maximum, minimum, and median concentrations, by month, for each compound are listed in table 3. Atrazine and nitrate were detected in every sample throughout the study period. Alachlor was detected in at least one sample each month throughout the study period except in January 1992. Cyanazine
was detected in at least one sample each month until November 1991, after which cyanazine was not detected.

The concentrations of atrazine and nitrate and the streamflow for April 12 through June 28, 1991, are shown in figure 4. Concentrations of atrazine reached a peak in mid-May. Atrazine concentrations exceeded the USEPA's maximum contaminant level of 3 \( \text{ug/L} \) for 13 days (May 15-27, 1991), and for shorter periods throughout April, May, and June 1991. Atrazine concentrations did not exceed 3 \( \text{ug/L} \) during the rest of the study.

Three distinct peaks in atrazine concentration occurred on May 9, 16, and 23, 1991 (fig. 4). Each of these peaks occurred concurrently with a peak in the discharge hydrograph. A discharge peak on April 19, 1991, exceeded the discharges on May 9, 16, and 23, but the atrazine-concentration peak associated with this discharge peak was only 4 \( \text{ug/L} \). Atrazine concentrations were low during this early spring runoff event because only about 9 percent of the corn planting was completed by April 21, 1991 (Illinois Agricultural Statistics Service, 1991). The percentage of the corn planting completed is a good indication of the percentage of atrazine applied, because atrazine is applied to about 76 percent of all corn acreage (Pike and others, 1990), and it usually is applied about the same time as planting. These results indicate that the highest concentrations of agricultural chemicals can be expected during the first few runoff events following chemical application, although, during 1990, high flows continued to flush atrazine from the fields in June even after planting was complete. The highest daily mean concentration of atrazine observed during the study period was 16.7 \( \text{ug/L} \) on May 16, 1991. The corresponding daily load for that day was 140 pounds, which is the largest calculated daily load.

Nitrate concentrations at the beginning of the study were at the USEPA maximum containment level of 10 \( \text{mg/L} \) and remained at or above this concentration, except for brief periods when dilution from runoff lowered the concentrations, until June 11, 1991; at this time the nitrate concentration decreased with a reduction in streamflow and remained below the MCL until December 1991, when the nitrate concentration again exceeded 10 \( \text{mg/L} \) until the end of the study.

### Table 3. Summary of agricultural chemical concentrations by month, in the Sangamon River at Monticello, Illinois, April 1991–March 1992

<table>
<thead>
<tr>
<th>Month</th>
<th>Number of samples</th>
<th>ATRAZINE (ug/L)</th>
<th>CYANAZINE (ug/L)</th>
<th>ALACHLOR (ug/L)</th>
<th>NITRATE (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>maximum</td>
<td>minimum</td>
<td>median</td>
<td>maximum</td>
</tr>
<tr>
<td>April</td>
<td>11</td>
<td>6.0</td>
<td>0.11</td>
<td>2.1</td>
<td>2.3</td>
</tr>
<tr>
<td>May</td>
<td>89</td>
<td>21.7</td>
<td>7.5</td>
<td>16</td>
<td>3.1</td>
</tr>
<tr>
<td>June</td>
<td>22</td>
<td>31.3</td>
<td>13.1</td>
<td>13</td>
<td>1.3</td>
</tr>
<tr>
<td>July</td>
<td>26</td>
<td>31.3</td>
<td>13.1</td>
<td>13</td>
<td>1.3</td>
</tr>
<tr>
<td>August</td>
<td>22</td>
<td>1.0</td>
<td>12.4</td>
<td>12</td>
<td>1.2</td>
</tr>
<tr>
<td>September</td>
<td>6</td>
<td>27.0</td>
<td>0.14</td>
<td>0.07</td>
<td>0.07</td>
</tr>
<tr>
<td>October</td>
<td>12</td>
<td>1.1</td>
<td>0.58</td>
<td>0.33</td>
<td>0.10</td>
</tr>
<tr>
<td>November</td>
<td>2</td>
<td>0.9</td>
<td>--</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>December</td>
<td>2</td>
<td>0.39</td>
<td>0.18</td>
<td>0.29</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>January</td>
<td>2</td>
<td>0.18</td>
<td>0.13</td>
<td>0.16</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>February</td>
<td>5</td>
<td>0.35</td>
<td>0.10</td>
<td>0.21</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>March</td>
<td>5</td>
<td>0.26</td>
<td>0.10</td>
<td>0.11</td>
<td>&lt;0.05</td>
</tr>
</tbody>
</table>

Surface-water samples from the Sangamon River at Monticello, Ill., were collected from April 12, 1991, through March 25, 1992, and were analyzed for concentrations of selected herbicides and nitrate. Total load of each compound was calculated using concentration and streamflow data; these calculated masses were compared with masses calculated in an earlier study. Transport rates were largest in May 1991 for all compounds analyzed. The total mass of each compound transported was compared to estimated application totals in the drainage basin above Monticello. During the study period, 1,607 pounds of atrazine were transported by the river; this mass represents 1.4 percent of the total annual application of 113,700 pounds. The river transported 669 pounds of cyanazine—a mass equal to 1.6 percent of the total annual application of 41,900 pounds. About 353 pounds of alachlor were transported by the river (0.31 percent of the 112,300 pounds applied). About 12,100 tons of

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**SUMMARY**

Surface-water samples from the Sangamon River at Monticello, Ill., were collected from April 12, 1991, through March 25, 1992, and were analyzed for concentrations of selected herbicides and nitrate. Total load of each compound was calculated using concentration and streamflow data; these calculated masses were compared with masses calculated in an earlier study. Transport rates were largest in May 1991 for all compounds analyzed. The total mass of each compound transported was compared to estimated application totals in the drainage basin above Monticello. During the study period, 1,607 pounds of atrazine were transported by the river; this mass represents 1.4 percent of the total annual application of 113,700 pounds. The river transported 669 pounds of cyanazine—a mass equal to 1.6 percent of the total annual application of 41,900 pounds. About 353 pounds of alachlor were transported by the river (0.31 percent of the 112,300 pounds applied). About 12,100 tons of
nitrogen fertilizer were applied, and 3,393 tons of nitrate as nitrogen were transported by the river (28 percent of the total amount applied). However, other natural and human-derived sources of nitrate could have contributed to this total load.

The timing of chemical application and the quantity of rainfall and runoff after herbicide application affected their concentrations. Herbicide concentrations peaked in early spring during storms after the herbicides were applied. Peak concentrations of atrazine, cyanazine, and alachlor occurred in May; these concentrations were 21, 16, and 8.8 µg/L, respectively. Nitrate concentrations were at or above the USEPA MCL of 10 mg/L from the beginning of the study period until June 11, 1991, when nitrate concentrations decreased to below the maximum containment level until November 1991 because of reduced streamflow.

Nitrate concentrations again exceeded 10 mg/L from December 1991 until the end of the study.

REFERENCES


U.S. Environmental Protection Agency, 1990, County-level fertilizer sales data: Office of Policy, Planning and Evaluation, PM-2221.


By A.D. Druliner1, D.A.Goolsby2, and M. Meyer3

Abstract

The West Fork of the Big Blue River in Nebraska drains a relatively flat basin of about 1,200 square miles in which the dominant land use is rowcrop agriculture. From April through July 1990 and April 1991 through March 1992 water samples were collected from the West Fork of the Big Blue River and analyzed principally for concentrations of selected herbicides, nitrite-nitrate, and suspended sediment. The purpose of the investigation was to determine the occurrence, temporal distribution, and persistence of selected herbicides and nitrite-nitrate in surface water within the West Fork of the Big Blue River Basin and to determine the effects of agricultural practices on the concentrations of these constituents.

Atrazine, alachlor, metolachlor, and cyanazine were the herbicides most commonly detected and present in the largest concentrations in the West Fork of the Big Blue River. Large concentrations of these herbicides were present in the river during the first major runoff events after spring chemical application in the fields. The magnitude of the concentrations diminished with successive runoff events. The maximum observed concentrations of the four herbicides were 116, 43, 26, and 8.6 micrograms per liter, respectively. Persistent concentrations of atrazine and some of its daughter products in base flow indicate that ground water is contributing atrazine to the river. On the basis of estimated herbicide application and estimated herbicide loads in the river in 1990 and 1991-92, about 0.4 to 1.3 percent of the total amount of herbicides applied are transported annually in the West Fork of the Big Blue River. The 3- to 4-fold increase in concentrations and loads of selected herbicides from the 1990 to 1991-92 sampling periods probably reflect the timing of chemical application and periods of major precipitation.

Nitrite-nitrate concentrations in the West Fork of the Big Blue averaged about 2.2 milligrams per liter and unlike herbicides showed limited variation between periods of high and low flow. The timing of nitrite-nitrate loads in the river indicates that the principal source of nitrogen is probably surface runoff of nitrogen fertilizer. Ground water also may be contributing to low-flow concentrations of nitrite-nitrate observed in the river. The load of nitrite-nitrate in the river is estimated to be about 0.6 percent of the nitrogen applied to croplands in the basin during each of the two years.

INTRODUCTION

Nebraska is one of many Midwestern States that relies on large quantities of chemical fertilizers and herbicides to sustain crop production. This is especially true for rowcrop production such as corn, sorghum, and soy beans. In 1987, more than 28 million pounds of active herbicidal ingredients (Baker and others, 1990) and about 752,000 tons of nitrogen chemicals (Nebraska Department of Agriculture, 1989) were applied to agricultural land in Nebraska.

1 U.S. Geological Survey, Lincoln, Nebraska.
To determine the potential effect of chemical fertilizers and herbicides on surface-water quality the U.S. Geological Survey, through its Toxic Substances Hydrology Program, began a series of regional studies in the Midwest in 1989. The first of the studies investigated 149 randomly selected streams throughout the Midwest that were sampled three times during 1989 for the presence of agricultural chemicals (Goolsby and others, 1991). The study revealed large concentrations of four herbicides—-atrazine, alachlor, cyanazine, and metolachlor—in storm runoff at most sampling sites following the application of herbicides in the spring.

The West Fork of the Big Blue River, which is located in southeastern Nebraska, was among nine sites that were selected for detailed study in 1990 and 1991 (Goolsby and others, 1991). The principal objectives of detailed study were to determine the occurrence, temporal distributions, and persistence of selected herbicides, nitrite-nitrate, and other related constituents in the surface water and to determine the effects of agricultural practices on concentrations of these chemicals in the surface water. This paper summarizes some of those findings for the West Fork of the Big Blue River.

**DESCRIPTION OF THE STUDY AREA**

The basin drained by the West Fork of the Big Blue River is located in the southeastern part of
Nebraska (fig. 1), in a region of relatively flat uplands. The basin has an area of about 1,200 square miles and includes parts of eight counties. The average discharge for the 33 years (1958-present) of record from a gaging station just above the rivers' confluence with the Big Blue River is 185 ft³/s or 134,000 acre-ft/yr (Boohar and others, 1991). Typically the flow is less than 100 ft³/s until late March or April, when periodic thunderstorms and surface runoff can increase the discharge to 2,000 to 3,000 ft³/s. The river usually returns to low-flow conditions in either August or September. Ground-water discharge is the principal source of water in the river during low-flow conditions, although irrigation-return flows also can contribute to the river during the mid- to late summer.

Thick, loamy soils that formed from loess deposits mantle most of the basin. The dominant land use in the basin is agriculture. About 75 to 80 percent of the basin is planted in corn, sorghum, and soybeans. Crop acreages and estimates of nitrogen and selected herbicides used in the basin during the 1990 and 1991 growing seasons are shown in table 1. About 75 percent of the cropland in the basin is irrigated. Most of the irrigation water comes from the basin's nearly 5,000 registered irrigation wells. A limited amount of surface water from the West Fork of the Big Blue River is diverted for irrigation.

Table 1. Crop acreage and estimated agricultural-chemical use comparison for the West Fork of the Big Blue River Basin for the 1990 and 1991 growing season

<table>
<thead>
<tr>
<th>Crop</th>
<th>1990</th>
<th>1991</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corn (acres)</td>
<td>402,899</td>
<td>432,191</td>
</tr>
<tr>
<td>Sorghum (acres)</td>
<td>107,896</td>
<td>96,037</td>
</tr>
<tr>
<td>Soy beans (acres)</td>
<td>88,315</td>
<td>85,234</td>
</tr>
<tr>
<td>Atrazine (pounds)</td>
<td>511,000</td>
<td>528,000</td>
</tr>
<tr>
<td>Alachlor (pounds)</td>
<td>230,000</td>
<td>243,000</td>
</tr>
<tr>
<td>Metolachlor (pounds)</td>
<td>140,000</td>
<td>143,000</td>
</tr>
<tr>
<td>Cyanazine (pounds)</td>
<td>124,000</td>
<td>144,000</td>
</tr>
<tr>
<td>Nitrogen (tons)</td>
<td>46,384</td>
<td>47,765</td>
</tr>
</tbody>
</table>

1 Estimates of total herbicide use were made by combining estimates of herbicide use for each major crop type in 1987 for the eastern and southeastern crop-reporting areas of Nebraska by Baker and others (1990) with estimates of acres planted to each crop type in 1987 (Nebraska Department of Agriculture, 1989). The herbicide-use figures were estimated by multiplying the rates as determined above by the number of acres planted in each of the major crops in the basin during 1990 and 1991.

2 Estimates of nitrogen use were made by multiplying the county nitrogen sales records for 1990 and for 1991 for each county in the basin (Nebraska Agricultural Statistics Service, 1991, 1992) by the percentage of that county included in the basin, and then totaling these values.

The broad-leaf pre-emergent herbicides, such as atrazine, alachlor, metolachlor, and cyanazine, are applied in corn fields at planting time by injection into the soil. Post-emergent herbicide applications frequently are made through center-pivot irrigation systems. Most of the nitrogen fertilizer is applied to fields cropped in corn as a preplant in March and April and is usually in the form of anhydrous ammonia that is injected into the soil. Urea-ammonium nitrate solutions also are used later in the spring and summer. Typically, rates of nitrogen fertilizer application on corn fields range from about 120 to 220 pounds of nitrogen per acre.

METHODS

Stream-water samples were collected by a combination of manual sampling and an automatic sampler from the West Fork of the Big Blue River from April through July 1990 and from March 1991 through April 1992 at a gaging station just above the confluence with the Big Blue River. The automatic sampler pumped samples from the river about every 2 to 4 hours when the river stage was 4 or more feet above base level. Water samples also were collected with the automatic sampler several times per week during periods of base flow using the sampler's manual mode. Manual samples were collected after late summer 1991. Daily discharge and suspended-sediment data also were collected.

During the 1990 sampling, all water samples were analyzed for specific conductance, pH, and concentrations of nitrite plus nitrate (nitrite-nitrate), and triazine and acetanilide herbicides. The triazine and acetanilide herbicides were analyzed using an enzyme-linked immunosorbent assay procedure (ELISA) (Pomes and others, 1991). Twenty percent of the herbicide samples also were analyzed by gas chromatography/mass spectrometry (GC/MS) using a method developed by Thurman and others (1990). The GC/MS analyses included atrazine, desethylatrazine, desisopropylatrazine, cyanazine, alachlor, metolachlor, metribuzin, simazine, propazine, prometon, prometryn, ametryn, and terbutryn. Atrazine concentrations were estimated for all samples from ELISA data through linear regression with GC/MS atrazine concentrations. Water samples collected in 1991 and 1992 were analyzed for the same constituents as in 1990; however, all samples were analyzed for herbicides by GC/MS. Samples also were analyzed for concentrations of dissolved nitrite-nitrate, ammonia, and orthophosphate.
RESULTS AND DISCUSSION

All of the herbicides analyzed, with the exception of terbutryn and prometryn, were present in water samples collected during high-flow conditions in the late spring and early summer for both the 1990 and 1991-92 sampling periods. The herbicides detected most frequently and in largest concentrations were atrazine, alachlor, metolachlor, and cyanazine with peak concentrations of 116, 43, 26, and 8.6 μg/L, respectively.

The changes in atrazine concentrations over time (fig 2) generally were similar to those observed for the other herbicides. The herbicide concentrations typically were near or below the applicable analytical detection limit prior to chemical application (usually mid-April to early May). Herbicide concentrations tended to peak almost simultaneously with peaks in stream discharge during the first major runoff event after chemical application. The height of the herbicide-concentration peaks diminished with each successive runoff event as the source of available herbicides decreased during the growing season. By late summer to early fall, concentrations of most of the herbicides decreased to below the detection limit. In the case of atrazine, small concentrations (0.1 to 0.5 μg/L) persisted during base flow, suggesting that ground-water discharge to the stream is responsible for these small atrazine concentrations.

Fluctuations in nitrite-nitrate concentrations were minor (<0.1 to 3.7 mg/L, as nitrogen) in response to changes in river discharge compared to the large fluctuations in herbicide concentrations that were observed. Nitrite-nitrate concentrations increased during periods of increased stream discharge associated with spring and summer runoff events (fig. 3). Nitrite-nitrate dilution during periods of very large stream discharge is probably responsible for the difference in times between some of the nitrite-nitrate and discharge peaks. The change in nitrite-nitrate concentrations over time suggests that much of the large nitrogen concentrations observed in the spring and early summer result from the transport of nitrogen fertilizer to the river in surface runoff. The late-summer decline in nitrite-nitrate is probably a combination of biological consumption of nutrients in the stream and diminished runoff and the amount of transported fertilizer available for transport to the river. The winter increase in nitrite-nitrate concentrations in the river during the second year of data collection probably reflects a combination of the discharge of ground water containing

![Figure 2. Temporal distribution of atrazine concentration and stream flow in the West Fork of the Big Blue River near Dorchester, Nebraska, March 1991 - March 1992.](image-url)
low concentrations of nitrite-nitrate into the river and reduced biological consumption of nutrients.

The temporal distribution of dissolved orthophosphate concentrations in water samples collected during the 1991-92 sampling period resembles a sine curve. Peak orthophosphate concentrations of about 0.4 mg/L (as phosphorous) occur in the late spring and early summer, followed by a decrease to about 0.1 mg/L during the fall, and a late increase to over 0.6 mg/L during the late winter. The peaks in orthophosphate concentration coincide with periods of phosphorous-fertilizer application in the basin. The large orthophosphate peak in the late winter is most likely the result of surface application of the fertilizer in the fall and winter rather than its incorporation in the soil as is done in the spring application.

Herbicide concentrations and, most notably, atrazine concentrations in the river were associated closely with suspended-sediment concentrations. Correlation coefficients for the log of atrazine concentration and for total herbicide concentrations, which is a sum of all herbicide concentrations for each sample, with a log of the suspended-sediment concentration were 0.675 and 0.731, respectively, for the period from March 1991 through April 1992. These results, coupled with the relatively moderate solubility of these herbicides in water (Weed Science Society of America, 1983), indicate that the herbicides are not strongly sorbed to the sediment and that they readily partition into the water during runoff events, thereby allowing both peaks in suspended sediment and dissolved herbicide concentrations to occur nearly simultaneously. Somewhat similar results were observed by Baker and Richards (1990) in Ohio rivers.

Comparison of the loads of atrazine and nitrite-nitrate during two 4-month periods (April through July) in 1990 and 1991 reveals a large increase in atrazine load (about 200 percent) in 1991 and a slight decrease in nitrite-nitrate load (about 9 percent) (table 2). During the same time period, the suspended-sediment load increased about 4 percent and the total stream discharge decreased about 10 percent.
Much of the difference in loads between the two sampling years can be explained by the relative timing of chemical application and major runoff events in the basin rather than actual amounts of precipitation received. In 1990, 15.5 inches of precipitation fell, but only modest runoff events occurred until mid-July, most of which generated stream discharges of only a few hundred ft$^3$/s. During one runoff event, the discharge exceeded 1,000 ft$^3$/s but the large discharge lasted only 2 days. Most of the high flow (>1,000 ft$^3$/s) that year occurred during the last 2 weeks of July when reduced amounts of herbicides were available for transport to the river. This resulted in only moderate concentrations and loads of atrazine and probably other herbicides being removed from the basin by streams in 1990. By contrast, all the runoff events in 1991 that generated stream discharges of 1,000 ft$^3$/s or more occurred in late May and early June--1 to 1 1/2 months earlier than in 1990. Consequently, large amounts of herbicides were available for transport to the river. The slight increase in suspended sediment load in 1991 also mirrors runoff from the early precipitation events when little ground cover crop was available to reduce soil erosion and surface runoff.

A comparison of the estimated amounts of selected herbicides and nitrogen applied to crop land in the basin (table 1) with removal of the loads from the basin in the West Fork of the Big Blue River, shows that relatively small amounts of parent chemicals are being removed by surface runoff. Only about 0.4 and 1.3 percent of the applied atrazine in the basin for 1990 and 1991, respectively, discharged to the river in runoff. About 0.6 percent of the estimated nitrogen applied within the basin during both years was accounted for in the streamflow. The parent compounds of alachlor, metolachlor, and cyanazine measured in the water samples collected during 1991 accounted for about 0.7, 1.1, and 0.2 percent, respectively, of total amounts of these chemicals applied in the basin. It should be noted, however, that significant amounts of herbicide metabolites, most of which were not analyzed for in this study, were most likely present in the stream (Baker and others, 1993), and that their consideration in the mass balance of herbicides would be expected to increase significantly the fraction of applied herbicides accounted for in the streamflow.

Analyses for desethylatrazine and desisopropylatrazine, two atrazine metabolites, were performed on water samples collected during the 1991 to 1992 sampling period. The concentrations of both metabolites increased during periods of increased discharge from mid-May through early June and tended to mirror atrazine concentrations observed during this time period, but at concentrations 3 to 50 times lower than those of atrazine. Desisopropylatrazine, which has a relatively short half-life, was detected primarily when peak atrazine concentrations were observed and was not detected after the end of September. Desethylatrazine, however, was detected throughout the sampling period and appeared to maintain a concentration of about 0.10 µg/L during periods of base flow. The desethylatrazine:atrazine ratio (DAR) in streamflow maintained an almost uniform value of about 0.36 except during the period of increased discharge and increased atrazine concentrations during May through early June when the median DAR value was 0.10. The persistence of low concentrations of desethyl atrazine and large DAR’s during periods of base flow suggest that ground water is contributing atrazine to the river in base flow. This conclusion is consistent with those of Thurman and others (1992) who found similar relations between low flow and desethylatrazine concentrations in other small midwestern river basins.

REFERENCES


Figure 4. Temporal distribution of desethylatrazine concentration, desethylatrazine to atrazine ratio (DAR) and stream flow in the West Fork of the Big Blue River near Dorchester, Nebraska, March 1991-March 1992.


Persistence of Herbicides in Selected Reservoirs in the Midwestern United States: Some Preliminary Results

By Donald A. Goolsby¹, William A. Battaglin¹, James D. Fallon², Diana S. Aga², Dana W. Kolpin³, and E. Michael Thurman²

Abstract

Preliminary results from a study of herbicides in 76 midwestern reservoirs show that some herbicides and metabolites of atrazine and alachlor are detected more frequently throughout the year in reservoirs than in streams. Except for a short period after application to cropland, herbicide concentrations also are generally higher in reservoirs than in streams. Herbicides or their metabolites were detected in 82 to 92 percent of the reservoirs sampled during four periods from late April through early November 1992. Atrazine was detected most frequently and in highest concentrations, followed by an alachlor metabolite (alachlor ethanesulfonic acid), and two atrazine metabolites (desethylatrazine and deisopropylatrazine). The longer persistence of some herbicides and metabolites in reservoirs than streams is attributed to longer half lives for these compounds in the water column than in the soil where concentrations of organic matter and microorganisms are much higher and contribute to rapid biodegradation of herbicides. A second contributing factor is long-term storage of water in reservoirs that originates as spring and summer storm runoff from cropland and which contains high concentrations of herbicides.

INTRODUCTION

Reservoirs are an important part of hydrologic systems in the Midwestern United States. According to data compiled by Ruddy and others (1990), about 440 large reservoirs (normal storage capacity greater than 5,000 acre-feet) in 11 upper Midwestern States discharge streamflow to the Mississippi River by way of tributaries. The primary function of these reservoirs is to impound surface water for many uses, including flood control, hydropower, recreation, and aquatic life habitat. These large reservoirs and numerous smaller reservoirs also can serve as sources of drinking water for public supplies. In addition to storing surface water, reservoirs also can store undesirable substances such as sediment and toxic chemicals including pesticides. Most of the sediment entering reservoirs is permanently trapped and deposited on the bottom of the reservoir. However, chemicals such as soluble herbicides generally remain in the water column and are stored only temporarily until they are flushed from the reservoir or removed from solution by biotic and abiotic processes.

Storage of herbicides is a potential problem in reservoirs that receive drainage from agricultural areas in the upper Midwest. Recent studies by the U.S. Geological Survey (USGS) (Thurman and others, 1991, 1992; Goolsby and others, 1991) have shown that most streams in the upper Midwest contain herbicides at some time during the year. Large quantities of herbicides are flushed from agricultural fields each spring and summer during rainfall following application of herbicides. Median concentrations of the herbicides atrazine, alachlor, cyanazine, and metolachlor in streams increased by at least an order of magnitude from March and April 1989 to May and June 1989.

For example, the median concentrations of herbicides in Midwestern streams, in 1989, ranged from less than 0.3 μg/L before planting to as much as 3 μg/L after planting, and the maximum concentrations in a few streams reached 100 μg/L (Thurman and others, 1991). During late spring and early summer, concentrations of atrazine can exceed the U.S. Environmental Protection Agency's regulated levels for drinking water, which are 3 μg/L. The longer persistence of some herbicides and metabolites in reservoirs than streams is attributed to longer half lives for these compounds in the water column than in the soil, where concentrations of organic matter and microorganisms are much higher and contribute to rapid biodegradation of herbicides.

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³U.S. Geological Survey, Iowa City, Iowa
Protection Agency's maximum contaminant level (MCL) for drinking water of 3 μg/L for several weeks to several months in both small streams and large rivers, such as the Mississippi River.

Because reservoirs collect and store water, they can be affected by storm runoff that contains large concentrations of herbicides for a much longer period of time than the streams that supply the reservoirs (Stamer and Zelt, 1992). This can substantially affect the water quality of streams downstream from reservoirs. The length of time that reservoirs discharge water with elevated concentrations of herbicides depends on a number of factors including residence time of water in the reservoir, timing of inflow to the reservoir, land use and herbicide use in the contributing drainage area, and the timing and intensity of rainfall. Unregulated streams exhibit the flush effect (Thurman and others, 1991) which can produce high concentrations of herbicides for short periods of time. In contrast, peak concentrations of herbicides in streams regulated by reservoirs are much lower, but elevated concentrations (near or above MCLs) can persist for much longer periods of time. Often, area and Zelt (1992) have shown that atrazine concentrations in Perry Lake, Kans., remained near or above the MCL of 3 μg/L from March 1989 through October 1989 and above 1 μg/L through February 1990, whereas atrazine concentrations in the principal tributary to Perry Lake exceeded the MCL for only a few months in late spring. However, atrazine concentrations in some of the samples from tributaries exceeded 10 μg/L during this period and much of the water in Perry Lake was replaced with containing these atrazine concentrations. Because little additional inflow to Perry Lake occurred after early summer, this “herbicide rich” water was stored in the reservoir until the next spring, when the cycle was repeated.

The process of storage and attenuation of herbicides documented in Perry Lake likely occurs in most other Midwestern reservoirs to a greater or lesser degree depending on physical and hydrologic characteristics of the reservoirs and land use in the reservoir drainage basin. Atrazine concentrations in mid-winter samples during 1990-92 from several large reservoirs in Illinois, Iowa, Kansas, Minnesota, Missouri, Nebraska, North Dakota, Ohio, South Dakota, and Wisconsin) that drain to the Ohio, Upper Mississippi, and Lower Missouri Rivers. This area comprises about 450,000 mi² and is virtually the same area covered by the 1989-90 reconnaissance for herbicides in streams (Thurman and others, 1991; 1992).

The primary objectives of the study are to (1) determine the occurrence and temporal distribution of selected herbicides and herbicide metabolites in the outflow from selected reservoirs in the upper Midwest, and (2) determine if the persistence of large concentrations (greater than about 1 μg/L) of herbicides in reservoir outflow can be quantified on the basis of reservoir and drainage-basin characteristics, hydrology, land use, herbicide use, and climate. Some specific hypotheses to be tested are--

1. Herbicides will be detected in Midwestern reservoirs for a longer period of time than in unregulated streams, but peak concentrations will be lower in the reservoirs than in these streams.

2. The duration of herbicide concentrations in reservoir outflow above a threshold value can be explained (statistical model) by reservoir and drainage-basin characteristics, land use, herbicide use, rainfall (intensity, timing and amount), and...
Table 1. Atrazine concentrations in water samples from selected midwestern reservoirs during winter months, 1990-92

<table>
<thead>
<tr>
<th>Reservoir</th>
<th>Sample date</th>
<th>Vol/DA (acre-ft/acre)</th>
<th>Atrazine concentration by GC (µg/L)</th>
<th>Atrazine concentration by ELISA (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Illinois</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carlyle Lake outflow</td>
<td>1-3-92</td>
<td>0.14</td>
<td>--</td>
<td>2.3</td>
</tr>
<tr>
<td>Lake Decatur outflow</td>
<td>1-8-92</td>
<td>0.05</td>
<td>--</td>
<td>0.2</td>
</tr>
<tr>
<td>Rend Lake Spillway</td>
<td>1-2-92</td>
<td>0.59</td>
<td>--</td>
<td>0.6</td>
</tr>
<tr>
<td>Lake Shelbyville outflow</td>
<td>1-8-92</td>
<td>0.31</td>
<td>--</td>
<td>1.1</td>
</tr>
<tr>
<td>Lake Springfield at Sugar Creek</td>
<td>1-30-92</td>
<td>0.34</td>
<td>--</td>
<td>2.5</td>
</tr>
<tr>
<td>Lake Springfield at Spaulding Dam</td>
<td>1-30-92</td>
<td>0.34</td>
<td>--</td>
<td>4.0</td>
</tr>
<tr>
<td><strong>Iowa</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coralville Lake</td>
<td>2-21-92</td>
<td>0.01</td>
<td>--</td>
<td>0.2</td>
</tr>
<tr>
<td>Corydon Reservoir</td>
<td>winter, 1992</td>
<td>--</td>
<td>--</td>
<td>10</td>
</tr>
<tr>
<td>Rathbun Reservoir</td>
<td>--12-90</td>
<td>0.58</td>
<td>3.7</td>
<td>--</td>
</tr>
<tr>
<td>Rathbun Reservoir</td>
<td>2-20-92</td>
<td>0.58</td>
<td>--</td>
<td>2.8</td>
</tr>
<tr>
<td>Red Rock Reservoir</td>
<td>2-12-92</td>
<td>0.01</td>
<td>--</td>
<td>0.2</td>
</tr>
<tr>
<td>Saylorville Lake</td>
<td>2-12-92</td>
<td>0.02</td>
<td>--</td>
<td>0.1</td>
</tr>
<tr>
<td><strong>Kansas</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Perry Lake</td>
<td>2-3-91</td>
<td>0.34</td>
<td>3.9</td>
<td>--</td>
</tr>
<tr>
<td><strong>Missouri</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Long Branch Reservoir</td>
<td>--12-90</td>
<td>0.50</td>
<td>2.0</td>
<td>--</td>
</tr>
<tr>
<td>Smithville Reservoir</td>
<td>--12-90</td>
<td>1.06</td>
<td>3.6</td>
<td>--</td>
</tr>
</tbody>
</table>

stability (half-lives) of individual herbicides. Consequently, the probability that a herbicide such as atrazine will persist in a reservoir all year above a specified concentration can be predicted.

3. The occurrence and concentrations of herbicides and herbicide metabolites in the anoxic hypolimnia of reservoirs during summer stratification differ from those in the aerobic epilimnia.

Reservoirs for study were selected from the reservoir data base compiled by Ruddy and others (1990). The principal criterion for selection of reservoirs was that data on reservoir volume and reservoir discharge must be obtainable so that the residence time of water in the reservoir and the timing of outflow can be determined. In addition, the reservoir outflow must be accessible for sampling. The reservoir data base was screened to determine which reservoirs met these
criteria. As a result of this screening, 74 of the 440 reservoirs in the reservoir data base were selected for sampling. Two additional reservoirs, Lakes Monona and Waubesa in Wisconsin, which form a chain of reservoirs receiving outflow from Lake Mendota, also

were selected. These three reservoirs will be treated as a single unit. Locations of these 76 reservoirs are shown in figure 1.

The outflow from each reservoir was sampled six times (approximately bimonthly) from April 1992
through March 1993, and a seventh time in mid-summer 1993. Samples are collected near the centroid of flow or other outflow point by methods that provide a representative sample of dissolved herbicides and nutrients in the outflow from the reservoir. During August 1992, herbicide samples, dissolved oxygen profiles, and temperature profiles were collected near the deepest point in 19 selected reservoirs to examine the effect, if any, of chemical stratification on herbicide concentrations. Herbicide samples were collected near the surface and near the bottom of each reservoir.

All samples are analyzed for 11 herbicides (alachlor, atrazine, ametryn, cyanazine, metolachlor, metribuzin, propazine, prometon, prometryn, simazine, and terbutryn) and at least 5 herbicide metabolites (desethylatrazine, desisopropylatrazine, deethylcyanazine, cyanazine amide, and deethylcyanazine amide) by gas chromatography/mass spectrometry (GC/MS). A metabolite of alachlor, [(2,6-diethylphenyl)(methoxymethyl) amino-2-oxoethane sulfonic acid], (ESA) is analyzed by immunoassay following isolation on C18 cartridges (Aga, 1994). Selected ESA samples are confirmed by high-performance liquid chromatography. Samples are also analyzed for nitrite, nitrate, ammonia, orthophosphate, and silica.

Ancillary data including land use, herbicide use, rainfall, and reservoir characteristics, are obtained from the following sources and stored in a geographic information system (GIS):

<table>
<thead>
<tr>
<th>Data Type</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Land Use</td>
<td>1987 Census of Agriculture data.</td>
</tr>
<tr>
<td>Rainfall</td>
<td>National Weather Service.</td>
</tr>
<tr>
<td>Reservoir characteristics</td>
<td>U.S. Geological Survey and Corps of Engineers data bases.</td>
</tr>
</tbody>
</table>

**PRELIMINARY RESULTS AND DISCUSSION**

Analytical results from samples collected during the first four sampling periods, during April through November 1992 indicate that a number of herbicides and/or their metabolites, are present in many Midwestern reservoirs for long periods of time. The four sampling periods include pre-planting (late April-early May), post-planting (late June-early July), late summer (late August-mid-September), and fall (mid October-early November). Herbicides were detected in 82 to 92 percent of the 76 reservoirs during all four sampling periods. Four compounds (atrazine, desethylatrazine, desisopropylatrazine, and metolachlor) were detected in more than half the reservoirs during the fall (October-November sampling; table 2), whereas only atrazine was detected in more than one half the streams sampled in the fall of 1989 (table 2). One of the most notable differences between the occurrence of herbicides in reservoirs and streams is the much higher frequency of detection of cyanazine and desisopropylatrazine in reservoirs. A possible explanation (hypothesis) for this observation is that these two compounds are much more stable in the water column of lake and streams than in soil, where organic matter and microorganisms promote rapid biodegradation. Consequently, late spring and summer runoff can flush large amounts of these two compounds into reservoirs, where they can persist in the water column for long periods of time. Neither cyanazine nor desisopropylatrazine was detected in streams during the fall (table 2) because these compounds are no longer present in significant amounts on the agricultural fields where they were applied. This hypothesis points to the need for data on the half-lives of herbicides and insecticides in water. Virtually all available data on the half lives of herbicides are for soils. Water-column-half lives are particularly important with regard to the persistence of herbicides in reservoirs, lakes, and estuarine systems.

The spatial distribution of the detections of herbicides and metabolites in the 76 reservoirs is shown in figures 2 and 3 for the four sampling periods. These figures also show which reservoirs contained herbicides in concentrations that exceeded MCL’s and/or health advisories (HA’s) for drinking water. MCL’s apply to average annual concentrations and are legally enforceable under the 1986 Safe Drinking Water Act, whereas HA’s are not enforceable. Exceedence of MCL’s or HA’s is of concern because many Midwestern reservoirs are used for public water supply. Concentrations of one or more herbicides exceeded MCL’s or HA’s in 8 reservoirs during the first sampling period, in 16 reservoirs during the second sampling period (fig. 2), in 7 reservoirs in the third sampling period, and in 2 reservoirs during the fourth sampling period (fig. 3). More herbicides and metabolites were detected in reservoirs in areas where use of
Table 2. Herbicides analyzed and percent detections in Midwestern reservoirs during 1992, and in Midwestern streams during 1989

<table>
<thead>
<tr>
<th>Herbicide</th>
<th>Reporting limit (µg/L)</th>
<th>late April-mid-May</th>
<th>late June-early July</th>
<th>late August-early September</th>
<th>late October-early November</th>
<th>pre-application (N=55)</th>
<th>post-application (N=132)</th>
<th>fall low-flow (N=145)</th>
</tr>
</thead>
<tbody>
<tr>
<td>alachlor</td>
<td>0.05</td>
<td>36</td>
<td>48</td>
<td>26</td>
<td>16</td>
<td>18</td>
<td>86</td>
<td>12</td>
</tr>
<tr>
<td>ametryn</td>
<td>0.05</td>
<td>0</td>
<td>1</td>
<td>3</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>atrazine</td>
<td>0.05</td>
<td>72</td>
<td>92</td>
<td>86</td>
<td>80</td>
<td>91</td>
<td>98</td>
<td>76</td>
</tr>
<tr>
<td>cyanazine</td>
<td>0.05</td>
<td>49</td>
<td>65</td>
<td>56</td>
<td>46</td>
<td>--</td>
<td>--</td>
<td>--</td>
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<td>77</td>
<td>64</td>
<td>--</td>
<td>--</td>
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</tr>
</tbody>
</table>

1 Reporting limit for Midwestern streams in 1989 was 0.2 µg/L. Percent detections for both reporting limits are given for data from 76 Midwestern reservoirs.

Herbicides is most intense—that is, the area from eastern Kansas and Nebraska to Ohio (figs. 2 and 3).

One of the most significant findings from this study to date is the abundance and persistence of herbicide metabolites in reservoirs. Data are presently available from this study on two metabolites of atrazine (desethylatrazine and desisopropylatrazine) and one metabolite of alachlor, ethanesulfonic acid. The occurrence of atrazine metabolites in streams and their use as indicators of surface-water/ground-water interaction has been reported previously by Thurman and others (1991, 1992). The presence of ESA in ground water was recently reported by Baker and others (1993) and Kolpin and others (1993). However, the present reservoir study is believed to be the first systematic effort to investigate ESA in surface water. The frequency of detection was greatest for atrazine, followed by three metabolites, ESA, desethylatrazine, and desisopropylatrazine in the 76 reservoirs during the four sampling periods (table 2). The overall median concentrations of these four compounds followed the same order. Cyanazine, metolachlor, and alachlor were fifth, sixth, and seventh, respectively with respect to frequency of detection and median concentration. Previous studies have shown that the herbicide, alachlor is not very persistent in streams (Thurman and others, 1991; 1992; Goolsby and others, 1991) or in ground water (Kolpin and others, 1993). However, this does not appear to be the case for one of...
Late April through mid May

Late June through early July

Figure 2. Generalized distribution of herbicide detections in Midwestern reservoirs and reservoirs in which concentrations of one or more herbicides exceeded a U.S. Environmental Protection Agency maximum contaminant level or health-advisory level for drinking water during late April through mid May and late June through early July, 1992.
Figure 3. Generalized distribution of herbicide detections in Midwestern reservoirs and reservoirs in which concentrations of one or more herbicides exceeded a U.S. Environmental Protection Agency maximum contaminant level or health-advisory level for drinking water during late August through early September and late October through early November, 1992.
its metabolites, ESA, which apparently is both mobile and relatively persistent (stable) in surface water.

The temporal distribution of atrazine, alachlor, and three metabolites during the four reservoir sampling periods is shown in figure 4. Also shown for comparison purposes is the temporal distribution of these compounds (except ESA) during the 1989 reconnaissance of Midwestern streams (Thurman and others 1991; 1992). These results indicate that concentrations of atrazine and its metabolites in streams shortly after herbicide application are higher than in reservoirs. However, at other times of the year, concentrations are somewhat higher in the reservoirs, particularly concentrations of the two metabolites of atrazine. Desisopropylatrazine was detected infrequently in streams prior to application and not at all in the fall of the year (fig. 4). In contrast, this metabolite of atrazine was detected in 58 to 70 percent of all samples collected during the four reservoir-sampling periods. As hypothesized previously, the reason for this large difference in frequency of detection is probably the short half life for desisopropylatrazine in soil combined with its much longer half life in the water column, and long-term storage of this compound in the water mass within reservoirs.

With regard to alachlor there appears to be little difference between concentrations in streams and reservoirs except shortly after application when concentrations in streams are higher (fig. 4). Alachlor disappears rather quickly in streamflow and in reservoirs, consistent with data reported for Perry Lake in Kansas (Stamer and others, 1993). ESA appears to be a major soil metabolite of alachlor (Baker and others, 1993); however, it is not known whether significant degradation of alachlor to ESA occurs in the water column of streams and reservoirs. The ESA concentrations in reservoirs were similar during all four sampling periods (fig. 4).

Data on herbicide and nutrient concentrations, reservoir inflow and outflow (residence time), rainfall-patterns, pesticide use and land use will be available upon the completion of this study.
**Figure 4.** Temporal distribution of atrazine, alachlor, and three metabolites in midwestern reservoirs during 1992 and in midwestern streams during 1989.
REFERENCES


Determining the Relative Age, Transport, and Three-Dimensional Distribution of Atrazine in a Reservoir Using Immunoassay

By James D. Fallon and E.M. Thurman

Abstract

The age, transport, and distribution of atrazine in a reservoir were determined by enzyme-linked immunosorbent assay. A pulse of stormwater runoff containing atrazine concentrations as much as nine times greater than the U.S. Environmental Protection Agency Maximum Contaminant Level (MCL) for drinking water (the MCL for atrazine is based on an annual average concentration of 3.0 micrograms per liter) was monitored as it moved through Perry Lake, northeastern Kansas, during the 1992 growing season. The drainage basin of Perry Lake is the first Pesticide Management Area designated by the State of Kansas. The leading edge of the pulse marked the boundary and mixing zone between atrazine applied in previous years and freshly applied atrazine. Deethylatrazine-to-atrazine ratios (DAR) further defined the relative age of atrazine in the reservoir. Runoff entering the reservoir immediately after herbicide application was identified by its small DAR values (0.095 to 0.134). Water with increasing DAR values (0.135 to 0.254) entered the reservoir as the year progressed and gradually displaced water with smaller DAR values. Four hundred and twenty (420) samples from four detailed reservoir surveys (pre-application, post-application, summer, and autumn) were analyzed by immunoassay to determine the distribution of herbicide concentrations in the reservoir. Also, weekly samples were collected from four fixed sites located upstream, within, and downstream from the reservoir. One hundred (100) of these samples were analyzed by gas chromatography/mass spectrometry to confirm immunoassay results and to determine deethylatrazine and deisopropylatrazine concentrations. A combination of immunoassay and DAR values could prove useful in developing reservoir-release strategies to mitigate atrazine concentrations in reservoirs and their outflows.

INTRODUCTION

Effects of herbicides on reservoir-water quality are not well known. Reservoirs are an important component of the supply and management of water resources in the midwestern United States. Their uses include drinking- and irrigation-water sources, flood control, recreation, and wildlife habitat. Reservoir-water quality is critical to many of these uses, especially drinking water. Many reservoirs used for drinking water drain basins whose primary land use is crop production. Herbicides generally are available for transport from agricultural areas into downstream reservoirs, and previous studies of stream water have shown that unregulated spring runoff can contain large concentrations of herbicides after their application. Furthermore, herbicide concentrations in streams have been shown to exceed the U.S. Environmental Protection Agency's MCL for drinking water for as long as 2 to 3 months during the crop-growing season (Goolsby and others, 1991; Thurman and others, 1991). Because reservoirs are designed to retain water, whether for flood control or water supply, they also
may retain herbicides. In the Midwest, water from spring runoff often is held to attenuate spring flood peaks and to store water for use later in the year. This herbicide-laden water is released slowly, increasing herbicide concentrations downstream for a longer period of time than would normally be expected.

In northeastern Kansas, concern about concentrations of atrazine in water from the Delaware River, which supplies Perry Lake, prompted establishment of the first Pesticide Management Area in the State (Carole Jordan, Kansas State Board of Agriculture, written commun., March 30, 1992). Perry Lake is a Federal reservoir with a storage volume of 277 x 10^6 m^3 used for flood control, drinking water, recreation, and wildlife habitat. Conservative atrazine-application practices were exercised voluntarily in the basin with the goal of decreasing atrazine concentrations in stream water and in Perry Lake.

This paper briefly describes the transport and three-dimensional distribution of atrazine in Perry Lake at a more detailed spatial scale than previously attempted using enzyme-linked immunosorbent assay (ELISA). ELISA was used as an accurate, fast, and inexpensive analytical method for determining the concentrations of herbicides, such as atrazine. This method allows a much larger number of samples to be analyzed than would be economically feasible using conventional methods, such as gas chromatography/mass spectrometry (GC/MS). Furthermore, this paper describes a test of the hypothesis that, by using GC/MS to analyze a subset of the ELISA samples, the deethylatrazine-to-atrazine ratio, or DAR, (Thurman and others, 1991), could be used to improve definition of the age of atrazine in a reservoir.

**SAMPLE COLLECTION**

Four synoptic surveys were conducted on Perry Lake from March 30 to September 22, 1992. Water samples were collected to assess the three-dimensional distribution of atrazine and two metabolites, deethylatrazine and deisopropylatrazine. Synoptic surveys were conducted on the following dates: a pre-application survey, March 30 through April 10, 1992; a first-flush, post-application survey, June 16-25, 1992; a summer survey, August 3 and 4, 1992, and a fall survey, September 16-22, 1992. The first two synoptic surveys were the most detailed, with 200 water samples collected during each survey from various depths at 100 sites throughout the reservoir. After these two surveys, it was apparent that atrazine concentrations varied more along the length of the reservoir than across the width. As a result, only about 40 samples were collected for the third survey from 25 sites along the north-south axis of the reservoir. No significant changes in atrazine concentration with depth were detected.

Sampling sites for the first two surveys were selected randomly from 500-m^2 grid cells (fig. 1A). When the water depth was less than 7.5 m, only one point in the water column was sampled. If the depth exceeded 7.5 m, two or more discrete samples were collected from different depths in the water column. Discrete analytical results from each depth within a cell were averaged together to produce figures 1 and 2. Water samples were collected with a Kemmerer sampler at selected intervals in the water column. Sample water was poured directly from the Kemmerer sampler into baked, 125-mL glass bottles and chilled.

**ANALYTICAL METHODS**

The immunoassay method used in this study was described previously (Thurman and others, 1990; Pomes and others, 1991) with minor differences in the arrangement of the samples and the rotation speed (200 revolutions per minute was used) during incubation. Triazine microtitre-plate kits used for the immunoassay contained polyclonal antibodies coated to the inside of the test-plate cell walls. Triazine-herbicide molecules in the water sample competed with atrazine-enzyme conjugate molecules for binding sites on the antibodies. The enzyme conjugate consisted of atrazine molecules covalently bonded to horseradish peroxidase (Bushway and others, 1988). Theoretically an equal number of antibody sites was coated to each cell and an equal number of atrazine molecules in the enzyme conjugate was added to each cell, so the number of triazine molecules in the water sample was the determinate variable. If the number of triazine molecules in the water sample was small (that is, less than the number of enzyme-conjugate atrazine molecules), more enzyme-conjugate molecules would be able to bind to antibody receptor sites. If the number of triazine herbicide molecules in the water sample was large (that is, more than the number of enzyme-conjugate atrazine molecules), the molecules would preempt the enzyme-conjugate atrazine molecules from bonding to antibody-receptor sites.
Figure 1. Mean concentrations of triazines from (A) pre-application, (B) first-flush, and (C) summer surveys at Perry Lake, northeastern Kansas.
All unfiltered samples were analyzed in the laboratory for triazine compounds by ELISA. Twenty-five percent of the samples were analyzed by GC/MS for confirmation of ELISA results and determination of atrazine metabolite concentrations. Water samples for confirmation of ELISA results and the determination of concentrations of deethylatrazine and deisopropylatrazine were analyzed by GC/MS by the method of Meyer and others (1993). Samples were filtered through a 0.7-μm glass-fiber filter into baked, 125-mL glass bottles. Analytes were extracted robotically from solution with solid-phase extraction cartridges. Eluates then were reduced to a volume of approximately 100 μL and transferred into 200-μL glass-lined polystyrene vials for GC/MS analysis.

RESULTS

Atrazine concentrations from the pre-application survey ranged from less than 1.0 μg/L at the upstream end of Perry Lake to 3.0-5.0 μg/L at the downstream end (fig. 1A). A gradual concentration change was identified throughout the length of the reservoir. In contrast, the first-flush survey showed the largest atrazine concentrations (5.0-25 μg/L) in the upstream end of the reservoir (fig. 1B). Atrazine concentrations in the remainder of the reservoir varied from 2.0-5.0 μg/L. The summer survey identified smaller atrazine concentrations (1.0-3.0 μg/L) entering the reservoir, and larger concentrations of atrazine (3.0-5.0 μg/L) in the downstream three-fourths of the reservoir (fig. 1C). No significant changes in atrazine concentration with depth were measured in any of the synoptic surveys. GC/MS analyses indicated that other triazines known to cross react with the immunoassay antibodies (Thurman and others, 1990) were not present or were insignificant, confirming that all of the triazine concentrations determined by immunoassay were attributable to atrazine.

DAR values were used to improve definition of the age of the atrazine and to track the water's movement through the reservoir. Atrazine does not readily metabolize in surface water. A small DAR value (less than 0.100) indicated that atrazine was flushed from the field immediately after application because of the limited time it would have to metabolize into deethylatrazine. The longer the atrazine remained on the field before being flushed off, the larger the DAR values. Thurman and others (1991) found that surface-water samples from the midwestern United States had DAR values of 0.3 in preplant samples, <0.1 in postplant samples, and 0.4 in the harvest samples.

DAR values were found to be inversely proportional to atrazine concentrations. The respective locations of small and large DAR values reversed from the pre-application survey to the post-application survey. During the pre-application survey, DAR values were largest (0.215-0.294) at the upstream end of the reservoir (fig. 2A). This indicated that the most recent pulse of water to enter the reservoir was the previous year's post-harvest surface-water runoff. The downstream end of the reservoir had the smallest DAR values (0.175-0.214), indicating this water had entered the reservoir during the previous growing season. During the post-application survey, the smallest DAR values (0.095-0.134) were found in the upstream half of the reservoir, and the largest DAR values (0.135-0.174) were found in the downstream half (fig. 2B). The smallest DAR values at the upstream end probably were from spring field runoff immediately after atrazine application which entered the upstream end of the reservoir as a pulse. In the summer survey, small DAR values were found in the downstream end of the reservoir and the outflow, whereas larger DAR values (0.135 - 0.174) were found entering the upper two-thirds of the reservoir (fig. 2C). No significant changes in DAR values with depth were observed in any of the synoptic surveys.

CONCLUSIONS

ELISA is an efficient and practical method for determining atrazine concentrations in reservoirs for large numbers of samples. Furthermore, by coupling ELISA with GC/MS on a small subset of samples, analytical results can be confirmed and relations among parent and metabolite compounds may be more readily explored. In this study, detailed spatial resolution of atrazine concentrations in reservoir water were determined by ELISA. Increases in atrazine concentration in the reservoir were detected following the first significant runoff after herbicide application. When data were combined with the subset of DAR values, analyses were proven to be effective in studying the transport of atrazine through Perry Lake. Also, an inverse relation was observed between the atrazine concentration in reservoir water and the DAR value. Similar relations may exist for other herbicides and their metabolites. These relations may be useful in assessing the water quality of reservoirs.
Figure 2. Deethylatrazine-to-atrazine ratios from (A) pre-application, (B) first-flush, and (C) summer surveys at Perry Lake, northeastern Kansas.
REFERENCES


By Dana W. Kolpin¹, Donald A. Goolsby², Diana S. Aga³, Jana L. Iverson², and E. Michael Thurman³

Abstract

Selected pesticides and metabolites were examined in near-surface aquifers in the corn- and soybean-producing region of the midcontinental United States to determine their hydrogeologic, spatial, and seasonal distribution. At least one herbicide or atrazine metabolite was detected in 28.4 percent of the 303 wells sampled during the spring and late summer of 1991. During 1991, deethylatrazine was the most frequently detected compound followed by atrazine, deisopropylatrazine, and prometon. No herbicide concentration exceeded the U.S. Environmental Protection Agency’s maximum contaminant levels for drinking water. During 1991, the highest frequency of herbicide detection was in the western part of the study region and lowest frequency of detection was in the eastern part of the study region. Unconsolidated aquifers were found to be more susceptible to herbicide contamination than bedrock aquifers on the basis of results of the 1991 study. During the summer of 1992, additional water samples were collected from 101 wells to examine the occurrence of agricultural chemicals not analyzed during the previous year. Water from 62 percent of the resampled wells had detectable concentrations of either a pesticide or pesticide metabolite; 27 different compounds were detected. During the 1992 study, five of the six most frequently detected compounds were herbicide metabolites.

INTRODUCTION

Almost 60 percent of the pesticides (Gianessi and Puffer, 1990) and fertilizers (U.S. Environmental Protection Agency, 1990) used in the United States are applied in the Midcontinent to enhance crop yields. Because of the potential for these contaminants to affect the quality of water resources, the Midcontinent has become a focus for research on agricultural-chemical contamination in all parts of the environment including streams, reservoirs, ground water, and rainfall. In 1991, the U.S. Geological Survey (USGS) through its Toxics Substances Hydrology Program, began a ground-water-reconnaissance of agricultural-chemical contamination in aquifers located within 15 m of the land surface (near-surface) in the midcontinental United States. Near-surface aquifers represent hydrogeologic settings that have the greatest potential for herbicide contamination. The objectives of this reconnaissance are to (1) determine the hydrogeologic, spatial, and seasonal distribution of agricultural chemicals in near-surface aquifers of the midcontinent; (2) determine statistical relations between the occurrence of agricultural chemicals and selected human and natural factors; and (3) collect data on pesticides and their metabolites in ground water from geographic areas where few data previously were available.

Because of questions generated by results of the 1991 sampling, additional data were collected during July and August 1992. The major objective of the additional sampling was to determine why reportable herbicide concentrations were not measured in more

¹U.S. Geological Survey, Iowa City, Iowa
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than 70 percent of the near-surface aquifers sampled in 1991. Possible explanations include the following: The wells sampled produce "old" water, which would not be expected to contain herbicides; herbicides are present in many of these aquifers but at concentrations below the reporting limits available during the 1991 study; herbicides are present but are compounds that were not examined during 1991; and the herbicide metabolites might be more persistent and mobile than their parent compounds and are present in the aquifers sampled. To test these hypotheses, the number of compounds analyzed for during 1992 was increased and included additional herbicides and selected metabolites, insecticides and selected metabolites, detergents, volatile organic compounds, and surfactants. Only the results for pesticides and pesticide metabolites are discussed in this paper.

This paper was previously published (Kolpin and others, 1993b) and describes results of a regional reconnaissance of selected agricultural chemicals in near-surface aquifers that was conducted during 1991, including some initial results from the continued investigation of agricultural chemicals in near-surface aquifers conducted during 1992. A comprehensive discussion of the data and interpretive results derived from the 1991 reconnaissance study is presented in other USGS reports. (Kolpin and others, 1993a; Kolpin and others, 1994).

STUDY DESIGN AND METHODS

Wells sampled during 1991 (fig. 1) were selected to ensure that sites were geographically and hydrogeologically representative of near-surface aquifers in the corn- and soybean-producing region of the Midcontinent. The wells were distributed geographically by State and hydrogeologically by aquifer class (unconsolidated as opposed to bedrock) and relative depth within the aquifer. A workplan outlining the design and plan for well selection, sample-collection protocol, and quality assurance was prepared to ensure the validity of collected data (Kolpin and Burkart, 1991). Most of the wells selected were sampled twice during 1991. A total of 299 herbicide analyses were obtained during March or April (preplanting); and 290 herbicide analyses were obtained during July or August (postplanting). Ancillary data on land use and other features near the wells were collected at the time of sampling.

In 1992, 101 wells were sampled during July or August after the application of pesticides. These wells were distributed geographically by State and hydrogeologically by aquifer class. This approach resulted in a widespread distribution of sampling sites across the Midcontinent (fig. 1).

All samples were collected by USGS personnel using equipment constructed of materials constructed of glass and stainless steel that would not leach or adsorb organic compounds. Decontamination procedures were implemented to prevent cross-contamination between wells and samples (Kolpin and Burkart, 1991). Wells were purged before sampling until pH, water temperature, and specific conductance stabilized. A quality-assurance program using a series of field blanks, field duplicates, and spikes verified effectiveness of the sampling protocol and the analytical procedures.

All samples collected during 1991 were analyzed for 11 herbicides and 2 atrazine metabolites by gas chromatography/mass spectrometry (GC/MS) (Thurman and others, 1990). This method had an analytical reporting limit of 0.05 μg/L (micrograms per liter). For the samples collected during 1992, several additional analytical methods also were used including a 1-liter solid-phase extraction GC/MS method (Steven D. Zaugg, U.S. Geological Survey, written commun., 1992). This method was used to analyze 47 pesticides with reporting limits as low as 0.001 μg/L. A total of 45 samples collected during 1992 were analyzed for chlorophenoxy acid herbicides (2,4-D for example) and DCPA. The selection of these 45 samples was biased toward wells with herbicides detected during 1991. Sixty-six samples were analyzed for an ethanesulfonate alachlor metabolite (ESA) by the method of Aga and others (1996). The selection of these 66 samples also was biased toward wells with herbicides detected during 1991.

RESULTS AND DISCUSSION

1991 Sampling

Herbicides or atrazine metabolites were detected in 28.4 percent of the wells sampled during the two collection periods in 1991 (table 1), but no concentrations exceeded U.S. Environmental Protection Agency (USEPA) maximum contaminant levels (MCL) for drinking water. The relatively low frequency of
herbicide detection in near-surface aquifers strongly contrasts with conditions observed in streams for this same region; herbicides were detected in nearly all of the streams sampled, and some of the concentrations exceeded an MCL (Thurman and others, 1992). Herbicides were not distributed uniformly in near-surface aquifers across the study region (fig. 2). The highest frequency of detection was observed in the extreme western part of the region; the lowest frequency of detection was observed in the eastern third of the region.

Data on herbicide metabolites are important to understand fully the occurrence, distribution, and fate of herbicides in the environment. The most frequently detected herbicide compound in water from wells sampled during the 1991 study was deethylatrazine (table 1). The frequency of atrazine-residue detection (atrazine plus deethylatrazine plus deisopropylatrazine) was 25.7 percent, whereas the frequency of atrazine detection alone was 20.8 percent. It is probable that the frequency of detection for other herbicide residues also would be larger if analyses for the metabolites of those herbicides were available. Consequently, if herbicide metabolites are not quantified, the effects

Table 1. Frequency of herbicide and atrazine-metabolite detection in water from wells sampled during the spring and summer of 1991

<table>
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<th>Compound</th>
<th>Maximum % detection</th>
<th>Maximum concentration (μg/L)</th>
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</thead>
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<tr>
<td>Any herbicide or metabolite</td>
<td>28.4</td>
<td>2.32</td>
</tr>
<tr>
<td>Deethylatrazine</td>
<td>21.4</td>
<td>2.32</td>
</tr>
<tr>
<td>Atrazine</td>
<td>20.8</td>
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</tr>
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<td>Deisopropylatrazine</td>
<td>7.6</td>
<td>1.17</td>
</tr>
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<td>Prometon</td>
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</tr>
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<td>Simazine</td>
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<td>0.27</td>
</tr>
<tr>
<td>Metribuzin</td>
<td>1.3</td>
<td>0.57</td>
</tr>
<tr>
<td>Cyanazine</td>
<td>1.3</td>
<td>0.68</td>
</tr>
</tbody>
</table>

1 Analytical reporting limit for all compounds is 0.05 μg/L.
The deethylatrazine-to-atrazine ratio (DAR) in water can provide information on the residence time of atrazine in the unsaturated zone (Thurman and others, 1992). Atrazine can be degraded by soil microorganisms to deethylatrazine and other metabolites. Below the soil zone, the effects of decreased amounts of available oxygen, reduced microbial activity, and reduced amounts of organic carbon combine to greatly reduce the biodegradation rates for atrazine (Dhileepan and Schnoor, 1992). Thus, slow infiltration through the soil results in larger DAR values than does rapid infiltration. Thurman and others (1992) reported DAR values in midwestern streams during 1989-90 generally were less than 0.1 during periods of spring runoff shortly after herbicide application but generally were 0.4 or larger in the fall during base-flow conditions. The median DAR value obtained from the 1991 ground-water reconnaissance (Kolpin and others, 1993a) was about 0.7 (fig. 3).

The frequency of herbicide detection in water from near-surface aquifers was significantly larger \((p = 0.002;\) Mann-Whitney test) in unconsolidated aquifers (28 percent) than in bedrock aquifers (17 percent). Unconsolidated aquifers might be more susceptible to herbicide contamination than bedrock aquifers for several reasons. First, most of the unconsolidated aquifers sampled, being alluvial in origin, have a long and narrow planar geometry; accordingly, paths of ground-water flow from recharge areas are much shorter than ground-water flow paths in the more laterally extensive bedrock aquifers sampled for this study. Second, there is a general absence of low-permeability material overlying the unconsolidated aquifers. About 78 percent of the unconsolidated aquifers sampled, but only 48 percent of the bedrock aquifers sampled, were under unconfined conditions. An aquifer that is confined in the vicinity of a properly constructed well is effectively isolated from the downward percolation of herbicides that might be applied near that well. Two lines of evidence support the conclusion that the...
unconsolidated aquifers are unconfined more often than bedrock aquifers and contain mostly local paths of ground-water flow. First, a significant difference in the frequency of herbicide detection between preplanting (22.6 percent) and postplanting (34.1 percent) sampling periods was found only in water samples from unconsolidated aquifers. Differences in water quality during such a short time would be expected only in aquifers that are recharged rapidly or that are located a short distance from its recharge area. Second, the median DAR was 0.57 for water samples from unconsolidated aquifers and 1.25 for water samples from bedrock aquifers. Because the DAR can indicate residence time in the unsaturated zone, the comparatively small DAR for unconsolidated aquifers again indicate that the recharge rates were generally more rapid than for the bedrock aquifers sampled.

The frequency of herbicide detection differed significantly (p = 0.001; Kruskal-Wallis test) among intervals of depth to the top of the aquifer material (0 to 3 m, 28.4 percent; 3 to 6 m, 29.9 percent; 6 to 9 m, 23.9 percent; 9 to 12 m, 16.9 percent; and greater than 12 m, 11.1 percent). Generally, the greater the depth to the top of the aquifer material, the smaller the frequency of herbicide detection. This vertical distance from land surface to the top of the aquifer material gives a general indication of the proximity of an aquifer to recharge source. The greater this distance, the greater the opportunity for processes such as transport, transformation, or sorption of chemicals to take place.

The percentage of land in corn or soybean production within a 3.2-km radius surrounding the wells did not appear to affect the frequency of herbicide detection. Although this lack of an association was unexpected, it could have been affected by either the selection criteria for this study, which required at least 25 percent of the land in a 3.2-km radius surrounding the wells be in corn or soybean production in the 1990 growing season, or that many herbicides being used in the Midcontinent and their respective metabolites were not analyzed during the 1991 study.

Figure 3. Deethylatrazine-to-atrazine ratios in water from wells sampled during 1991 and for the surface water reconnaissance, Midcontinental United States during 1989-90. (Thurman and others, 1992.)
The frequency of herbicide detection was related to crop irrigation. Water samples from wells located within 3.2 km of irrigated crops had almost double (35 percent) the frequency of herbicide detection than was observed in water samples from wells without nearby irrigation (19 percent). Almost 95 percent of the wells near irrigated areas were in unconsolidated aquifers, where some of the irrigation water typically recharges locally to aquifers. Under these conditions, irrigation could result in continuous leaching of chemicals to the aquifer throughout the irrigation season.

The frequency of herbicide detection was related to the proximity of a well to a stream. The frequency of herbicide detection in water samples from wells within 30 m of a stream was more than double (48 percent) that observed in water samples from wells with no stream nearby (22 percent). This difference can result from a hydrologic connection between aquifers and streams due to either natural or induced hydraulic gradients or a convergence of ground-water flow paths where ground water discharges to streams. Frequencies of detection and concentrations of herbicides are much larger in streams than in aquifers in the Midcontinent (Thurman and others, 1992). Thus, recharge to an aquifer by a stream could be a source of herbicide contamination to the aquifer (Squillace and others, 1993).

1992 Sampling

Herbicides, herbicide metabolites, or insecticides (table 2) were detected in water samples from 62 percent of the wells resampled during 1992. Most of these detections were at concentrations of less than 0.5 µg/L; some concentrations were in the parts per trillion range. No concentration exceeded a USEPA MCL for drinking water. Although concentrations of some of these compounds can be very low, even trace amounts can be important in identifying flow paths and transformation patterns in the hydrologic system, because these compounds are not present in the environment under natural conditions. The frequency of herbicide detection was much larger in 1992 than in 1991 because more herbicides and herbicide metabolites were analyzed (40 in 1992 as opposed to 13 in 1991); 20 insecticides were included in the suite of compounds analyzed; analytical reporting limits for many compounds were about an order of magnitude lower for the 1992 study than for the 1991 study; and the sample selection for some of the herbicides and herbicide metabolites analyzed for the 1992 study was biased toward wells where these compounds were detected during 1991.

A preliminary analysis of results indicates that the detections of pesticides in the 1992 study were much more evenly distributed across the Midcontinent (fig. 4) than determined from the 1991 sampling (fig. 2). In particular, spatial patterns of detections in the eastern part of the study region were similar to those in other parts of the region, in contrast to results from the 1991 study. The greater frequency of detection in the eastern part of the study region can be attributed to the lowered reporting limits for atrazine and simazine and to the analysis of alachlor metabolites. Spatial patterns of detections across the Midcontinent are apparent when specific compounds are examined. For example, more than 50 percent of the insecticide detections were in Nebraska and more than 60 percent of the simazine detections were in Ohio.

Data obtained from the 1992 sampling reinforces the importance of metabolite information to understand fully the occurrence, distribution, and fate of pesticides in the environment. Of the six most frequently detected pesticide compounds during 1992, five were herbicide metabolites (table 2). In addition to alachlor, two alachlor metabolites also were detected: 2,6-diethylanaline and ESA. ESA recently has been identified as a relatively persistent and mobile compound (Baker and others, 1993; Aga and others, 1996). Analytical results on alachlor and the two aforementioned metabolites were available from 66 samples. Of these samples, only about 8 percent contained detectable concentrations of alachlor; however, 21 percent contained detectable levels of 2,6-diethylanaline and 47 percent contained ESA. The detection frequency of alachlor-residue (alachlor plus 2,6-diethylanaline plus ESA) was 53 percent, or more than 5 times the detection frequency of the parent compound alone. Although no alachlor concentrations exceeded the USEPA MCL of 2.0 µg/L, 4.5 percent of alachlor-residue concentrations exceeded 2.0 µg/L, and 15 percent exceeded 1.0 µg/L. These results show how the effects of pesticides on the quality of water resources can be substantially underestimated without data on metabolites.
Table 2. Frequency of pesticide and pesticide metabolite detections in water from wells sampled during 1992, Midcontinental United States

<table>
<thead>
<tr>
<th>Compound</th>
<th>percent detection</th>
<th>Number of samples(^1)</th>
<th>Maximum concentration (µg/L)</th>
<th>Reporting limit (µg/L)(^2)</th>
<th>Action/use(^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Any pesticide or metabolite</td>
<td>62.0</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ESA</td>
<td>47.0</td>
<td>66</td>
<td>4.95</td>
<td>0.100</td>
<td>Herbicide metabolite (alachlor)</td>
</tr>
<tr>
<td>Atrazine</td>
<td>43.0</td>
<td>100</td>
<td>1.03</td>
<td>0.05</td>
<td>Selective herbicide: corn, sorghum</td>
</tr>
<tr>
<td>Deethylatrazine</td>
<td>31.0</td>
<td>100</td>
<td>1.79</td>
<td>0.015</td>
<td>Herbicide metabolite (atrazine)</td>
</tr>
<tr>
<td>Deisopropylatrazine</td>
<td>18.2</td>
<td>66</td>
<td>0.28</td>
<td>0.050</td>
<td>Herbicide metabolite (atrazine)</td>
</tr>
<tr>
<td>2,6-Diethylaniline</td>
<td>16.0</td>
<td>94</td>
<td>0.022</td>
<td>0.003</td>
<td>Herbicide metabolite (alachlor)</td>
</tr>
<tr>
<td>DCPA</td>
<td>15.6</td>
<td>45</td>
<td>2.22</td>
<td>0.10</td>
<td>Herbicide metabolite (dacthal)</td>
</tr>
<tr>
<td>Simazine</td>
<td>13.0</td>
<td>100</td>
<td>0.77</td>
<td>0.005</td>
<td>Selective herbicide: corn,</td>
</tr>
<tr>
<td>Metolachlor</td>
<td>11.0</td>
<td>100</td>
<td>0.76</td>
<td>0.002</td>
<td>Selective herbicide: corn, sorghum, soybeans</td>
</tr>
<tr>
<td>Prometon</td>
<td>9.0</td>
<td>100</td>
<td>1.35</td>
<td>0.010</td>
<td>Nonselective herbicide</td>
</tr>
<tr>
<td>2,4-D</td>
<td>6.7</td>
<td>45</td>
<td>0.89</td>
<td>0.010</td>
<td>Selective herbicide: corn, sorghum, pasture</td>
</tr>
<tr>
<td>P,P' DDE</td>
<td>6.4</td>
<td>94</td>
<td>0.3</td>
<td>0.006</td>
<td>Insecticide metabolite (DDT)</td>
</tr>
<tr>
<td>Alachlor</td>
<td>5.0</td>
<td>100</td>
<td>0.99</td>
<td>0.002</td>
<td>Preemergent herbicide: corn, soybeans</td>
</tr>
<tr>
<td>Dicamba</td>
<td>4.4</td>
<td>45</td>
<td>0.01</td>
<td>0.010</td>
<td>Herbicide</td>
</tr>
<tr>
<td>Picloram</td>
<td>4.4</td>
<td>45</td>
<td>0.03</td>
<td>0.010</td>
<td>Systemic herbicide: deep-rooted plants</td>
</tr>
<tr>
<td>Chlorpyrifos</td>
<td>4.2</td>
<td>94</td>
<td>0.024</td>
<td>0.004</td>
<td>Insecticide: corn, soybeans</td>
</tr>
<tr>
<td>Ethalfluralin</td>
<td>3.2</td>
<td>94</td>
<td>0.014</td>
<td>0.004</td>
<td>Selective preemergence herbicide: soybeans</td>
</tr>
<tr>
<td>Cyanazine</td>
<td>3.0</td>
<td>100</td>
<td>0.02</td>
<td>0.008</td>
<td>Selective herbicide: corn</td>
</tr>
<tr>
<td>2,4,5-T</td>
<td>2.2</td>
<td>45</td>
<td>0.02</td>
<td>0.010</td>
<td>Discontinued herbicide</td>
</tr>
<tr>
<td>EPTC</td>
<td>2.1</td>
<td>94</td>
<td>0.03</td>
<td>0.002</td>
<td>Selective herbicide: corn</td>
</tr>
<tr>
<td>Trifluralin</td>
<td>2.1</td>
<td>94</td>
<td>0.016</td>
<td>0.003</td>
<td>Selective preemergence herbicide: soybeans</td>
</tr>
<tr>
<td>Triallate</td>
<td>2.1</td>
<td>94</td>
<td>0.007</td>
<td>0.001</td>
<td>Selective preemergence herbicide: wheat</td>
</tr>
<tr>
<td>Benfluralin</td>
<td>1.1</td>
<td>94</td>
<td>0.018</td>
<td>0.004</td>
<td>Herbicide: alfalfa, clover</td>
</tr>
<tr>
<td>Napropamide</td>
<td>1.1</td>
<td>94</td>
<td>0.008</td>
<td>0.003</td>
<td>Selective herbicide: orchards, tobacco</td>
</tr>
<tr>
<td>Pendimethalin</td>
<td>1.1</td>
<td>94</td>
<td>0.01</td>
<td>0.008</td>
<td>Selective herbicide: corn, soybeans</td>
</tr>
<tr>
<td>Propachlor</td>
<td>1.1</td>
<td>94</td>
<td>0.002</td>
<td>0.007</td>
<td>Herbicide</td>
</tr>
<tr>
<td>Tebuthiuron</td>
<td>1.1</td>
<td>94</td>
<td>0.05</td>
<td>0.010</td>
<td>Herbicide: noncropland areas, rangeland</td>
</tr>
<tr>
<td>Metribuzin</td>
<td>1.0</td>
<td>100</td>
<td>0.05</td>
<td>0.005</td>
<td>Herbicide: soybeans</td>
</tr>
</tbody>
</table>

\(^1\)When sample size is less than 94, the frequency of detection for that compound may be affected by the biased sample selection toward wells that had a herbicide detection during 1991

\(^2\)Reporting limits of compounds not detected: alpha BHC (0.002), ametryn (0.05), bentazon (0.10), butylate (0.002), carbaryl (0.01), carbofuran (0.01), 2,4-DP (0.01), dacthal (0.002), diazinon (0.002), dieldrin (0.002), dimethoate (0.02), disulfoton (0.017), ethoprop (0.003), fonofos (0.003), linuron (0.01), malathion (0.005), methyl parathion (0.008), methyl azinphos (0.005), molinate (.004), parathion (0.005), pebulate (0.005), permethrin (0.01), phorate (0.003), prometryn (0.05), pronamide (0.004), propargite (0.02), propanil (0.005), propazine (0.05), silvex (0.01), terbacil (0.01), terbufos (0.013), terbutryn (0.05), thiofencarb (0.002)

\(^3\)modified from Meister (1992)
SUMMARY

Herbicides or herbicide metabolites were detected in water samples from 28.4 percent of wells sampled in near-surface aquifers of the Midcontinent during 1991. During 1991, deethylatrazine was the most frequently detected compound followed by atrazine, deisopropylatrazine, and prometon. The highest frequency of detection was observed in the extreme western part of the region; the lowest frequency of detection was observed in the eastern third of the region. Unconsolidated aquifers were more susceptible to herbicide contamination than the bedrock aquifers sampled because of their general long and narrow planar geometry and the general absence of overlying confining units. The frequency of herbicide detection was inversely related to the depth to the top of the aquifer material. The greater this depth, the greater the opportunity for processes such as transport, transformation, and sorption of chemicals to occur. The frequency of herbicide detection almost doubled when crops were irrigated within 3.2 km of the well. The frequency of herbicide detection more than doubled when a well was within 30 m of a stream, possibly because of either natural or induced hydraulic gradients or from a convergence of ground-water flow paths near a stream.

During 1992, a pesticide or pesticide metabolite was detected in 62 percent of the 101 wells resampled. The greater frequency of detection during 1992 was caused by an increased number of herbicides and herbicide metabolites analyzed, inclusion of insecticides in the suite of compounds analyzed, analytical reporting limits for many compounds that were lower (about an order of magnitude) in 1992 than in 1991, and biasing the sample selection for some of the herbicides analyzed toward wells in which herbicides were detected during 1991. Herbicide detections in the 1992 study were much more evenly distributed across the region than in the 1991 study, probably because of the low reporting limits of atrazine and simazine and the analysis of alachlor metabolites.
Data on herbicide metabolites are important for a full understanding of the occurrence, distribution, and fate of herbicides in the environment. During 1991, the most frequently detected compound was deethylatrazine, and the frequency of atrazine-residue detection was greater than the frequency of atrazine detection alone. During the 1992 resampling, five of the six most frequently detected compounds were herbicide metabolites. The frequency of alachlor-residue detection was more than five times the frequency of alachlor detection alone. These results show how the affects of pesticides on the quality of water resources can be substantially underestimated without data on metabolites.

REFERENCES


Predicting Nitrate-Nitrogen and Atrazine Contamination in the High Plains Aquifer in Nebraska

By A.D. Druliner and T.S. McGrath

Abstract

Three statistical models, developed through the Toxic-Waste–Ground-Water Contamination Program of the U.S. Geological Survey, were used to predict the concentrations of nitrate-nitrogen and atrazine and the probability of atrazine detections in ground water in Buffalo and Hall Counties, south-central Nebraska. The models use a combination of hydrochemical, hydrologic, soils, and land-use explanatory variables, and ARC/INFO techniques to generate maps showing predicted concentrations of the selected contaminants. Confirmational testing of the models and comparison of maps of predicted concentrations to maps of observed concentrations showed that the statistical models were reasonable predictors of nitrate-nitrogen and atrazine concentrations in ground water of the High Plains aquifer in south-central Nebraska.

INTRODUCTION

Today, farmers in Nebraska, like farmers throughout most agricultural States across the Nation, rely on fertilizers and pesticides to maximize crop yields and to sustain productivity. Mineral fertilizers, such as nitrogen, and broadleaf herbicides, such as atrazine, have been applied annually over large areas of Nebraska for more than 30 years. In 1989, Nebraska farmers applied an estimated 662,000 tons of nitrogen (as N) fertilizers—an amount slightly less than amounts applied earlier in the decade (Nebraska Department of Agriculture, 1980; 1990). In 1987, an estimated 28.6 million pounds of herbicide was applied in Nebraska (Baker, and others, 1990)—an 18 percent increase over 1982 estimates even though planted acreages actually declined by about 13 percent during the 6-year period. As a result of the intensive use of agricultural chemicals (Gormly and Spalding, 1979), ground water in many areas of the State is contaminated with nitrate-nitrogen concentrations in excess of the U.S. Environmental Protection Agency’s (1991) maximum contamination level of 10 mg/L for drinking water and contains trace concentrations of atrazine (Exner and Spalding, 1990). However, not all ground water in areas of Nebraska where these chemicals are regularly used is contaminated to the same extent (Chen and Druliner, 1987), suggesting that one or more combinations of physical factors are affecting the transport of these contaminants to the ground water.

The U.S. Geological Survey conducted a nonpoint-source ground-water contamination study in Nebraska to investigate the relations among concentrations of nitrate-nitrogen and atrazine in ground water and quantifiable physical factors. During the first phase of the study, Chen and Druliner (1987) investigated the presence of selected agricultural chemicals in ground water in parts of the High Plains aquifer and performed a preliminary investigation of the effects of selected physical factors on ground-water contamination by nitrate-nitrogen and atrazine. One of the specific objectives of the second phase of the study was to develop techniques that could be used to recognize or predict areas of potential ground-water contamination by selected agricultural chemicals.

This paper describes three statistical models developed as part of the second phase of the study that relate nitrate-nitrogen and atrazine concentrations in ground water to hydrologic, land-use, and soils variables in Nebraska. The models are used to predict nitrate-nitrogen and atrazine concentrations and atrazine detections in ground water in Buffalo and Hall Counties, south-central Nebraska (area 1, fig. 1), and the predictions are compared to observed concentrations of nitrate-nitrogen and atrazine in ground water in the same area.

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SOUTH DAKOTA

US Geological Survey

SOUTH DAKOTA

Stake of Nebraska, 1984

Projection Albers Equal Area Conic projection

Projection Albers Equal Area Conic projection

Standard parallels 29°30' and 46°30', central meridian 98°

AREA UNDERLAIN BY HIGH PLAINS AQUIFER

BOUNDARY OF STUDY AREA

MODEL CONFIRMATION

STUDY AREA

WELL SAMPLED FOR WATER QUALITY

IRRIGATION WELLS USED FOR CONFIRMATION OF PREDICTIVE MODELS

Figure 1. Extent of the High Plains aquifer in Nebraska, the location of ground-water sampling sites in the six study areas, and the location of Merrick County.

APPRAOCH

Six study areas encompassing 12 counties of Nebraska were selected in an effort to investigate a variety of hydrologic, land-use, and soils factors that could affect ground-water contamination by agricultural chemicals (fig. 1). More than 70 explanatory variables were tentatively identified as possibly affecting ground-water contamination. Some examples of these variables are depth to water, average hydraulic conductivity, fertilizer application amounts, tillage type, soil slope, and soil permeability. Water-quality samples were collected from 268 irrigation, domestic, public, and stock wells in the six study areas during a 4-year period (1984-87). Data quantifying the explanatory variables were compiled for each of the 268 well sites and compared to nitrate-nitrogen concentrations in the ground water at each site. Similarly, data describing explanatory variables for 210 of the well sites were compared with atrazine concentrations in the ground water. Data for all six areas, as well as for single areas, were used to construct a variety of statistical models that could be used to predict areas of present or potential ground-water contamination.

DESCRIPTION OF STUDY AREAS

The six study areas contain from one to three counties each, and all are underlain by the High Plains aquifer (fig. 1). A variety of locations was selected to
provide a wide range of hydrochemical, hydrologic, soils, and land-use conditions in addition to targeting some areas of existing and potential ground-water contamination by agricultural chemicals. A brief description of the hydrology, land-use, and soils variables follows.

The High Plains aquifer is generally unconfined and consists of silt, sand, and sandstone of Tertiary Age with some calcareous cement and local zones of coarse sand and gravel and (or) overlying clay, silt, and sand of Quaternary age. In the six study areas, the High Plains aquifer is from 100 to 400 ft thick and is underlain by relatively impermeable clay of Cretaceous age. Recharge, chiefly from precipitation, occurs throughout most of the High Plains aquifer in the study areas. Additional recharge is provided by seasonal irrigation return flows, losing reaches of streams and rivers, and leakage from canals. Discharge from the aquifer in all areas occurs primarily through irrigation-well pumpage; secondary losses occur from evapotranspiration and ground-water discharge to streams, lakes, and canals.

The soils overlying the High Plains aquifer vary with the local topography and underlying geology. Soils in the study areas range from loamy, sandy soils in the Platte River Valley (areas 1 and 2) and adjacent to the Sand Hills (area 6) to clayey and silty soils in area 4 (Kuzila and others, 1990).

Irrigated corn is the dominant crop in five of the six areas and typically receives larger application amounts of nitrogen fertilizer and pesticides than other crops grown in Nebraska. Nitrogen most commonly is applied as anhydrous ammonia, which is usually injected into the ground prior to planting time. During the 1980's, nitrogen sales in the six study areas fluctuated from 100,000 to 150,000 tons/yr (Nebraska Department of Agriculture, 1980; 1990). The most commonly used pesticide on row crops in Nebraska is atrazine, a pre-emergent herbicide used to control broadleaf weeds in corn and sorghum. An estimated 13.4 million pounds of atrazine was applied in Nebraska in 1988 (Baker and others, 1990).

METHODS

Multiple linear-regression techniques as described by Minitab (1989) and SAS (1990) were used to generate statistical models with nitrate-nitrogen and atrazine concentrations as the dependent variables. Stepwise, stepwise forward, stepwise backwards, best-regression methods were used. In the Minitab stepwise-regression efforts, a minimum F-statistic of 1.8 was used to determine which explanatory variables would remain in the models even though all models containing explanatory variables with F-statistics less than 4 (and with T-ratio less than 2) were later rejected. The maximum R and R-squared techniques in SAS were designed to maximize the R-square values (percentage of explained variation) for each model by stepwise selection of explanatory variables, or by considering all combinations of explanatory variables, respectively. The Lillifores test (Iman and Conover, 1983) was used to ensure that the residuals for each of the representative models were normally distributed at the 95-percent confidence level. Plots of the residuals as a function of the predicted values were examined for each model to reveal trends that might indicate the presence of untested variables.

Logistic regression methods were used to develop models predicting the probability of atrazine detections in ground water with atrazine data that were converted to detect or nondetect values. Through a maximum-likelihood methodology, this technique produced multiple-regression models that predicted the probability of the presence or absence of the dependent variable at the specified threshold value. The goodness-of-fit for the logistic models was determined by comparing the percentages of correct and incorrect predictions rather than through coefficients of determination. Models were considered acceptable if they represented logically plausible relations with the explanatory variables and if the probability of exceeding the Chi-square statistic was less than 0.05 for each explanatory variable included in the model.

RESULTS

A number of multiple linear-regression models were produced with nitrate-nitrogen and atrazine concentrations as the dependent variables. Models were generated using data for all of the sampled areas, and other models used subsets of the data based on individual study areas. The best of these models explained from 50 to 68 percent of the variation (coefficient of determination) observed in the dependent variables. Logistic models using just atrazine concentrations as the dependent variables yielded predicted accuracies up to 81 percent when compared to the input data. Examples of these models are presented in table 1.
Table 1. Regression models used to predict concentrations of nitrate-nitrogen and atrazine and the probability of atrazine detections in ground water

<table>
<thead>
<tr>
<th>Explanatory variables</th>
<th>Regression coefficients</th>
<th>T-ratio</th>
<th>P-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept</td>
<td>21.890</td>
<td>2.00</td>
<td>0.047</td>
</tr>
<tr>
<td>Specific conductance</td>
<td>0.014902</td>
<td>6.01</td>
<td>0</td>
</tr>
<tr>
<td>Average hydraulic conductivity of the unsaturated zone</td>
<td>0.080430</td>
<td>4.72</td>
<td>0</td>
</tr>
<tr>
<td>Median well-completion date in 1-mile radius</td>
<td>-0.43650</td>
<td>1.96</td>
<td>0.050</td>
</tr>
<tr>
<td>Coefficient of determination = 0.68</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Model A: Nitrate-nitrogen concentration (multiple-linear regression)

<table>
<thead>
<tr>
<th>Explanatory variables</th>
<th>Regression coefficients</th>
<th>T-ratio</th>
<th>P-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept</td>
<td>-1.46360</td>
<td>-6.40</td>
<td>0</td>
</tr>
<tr>
<td>Nitrate-nitrogen concentration</td>
<td>0.0035944</td>
<td>6.05</td>
<td>0</td>
</tr>
<tr>
<td>Depth to water</td>
<td>-0.006926</td>
<td>2.52</td>
<td>0.015</td>
</tr>
<tr>
<td>Number irrigated acres in 1.7-mile radius</td>
<td>0.0007743</td>
<td>2.02</td>
<td>0.048</td>
</tr>
<tr>
<td>Coefficient of determination = 0.61</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Model B: Atrazine concentration (multiple-linear regression)

<table>
<thead>
<tr>
<th>Explanatory variables</th>
<th>Regression coefficients</th>
<th>Chi-square</th>
<th>P-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept</td>
<td>-5.6503</td>
<td>6.6052</td>
<td>0.010</td>
</tr>
<tr>
<td>Nitrate-nitrogen concentration</td>
<td>0.1822</td>
<td>14.3439</td>
<td>0</td>
</tr>
<tr>
<td>Water-table gradient</td>
<td>-959.1</td>
<td>11.0128</td>
<td>0.001</td>
</tr>
<tr>
<td>Percentage of clay in soil</td>
<td>-0.0559</td>
<td>4.8374</td>
<td>0.028</td>
</tr>
<tr>
<td>Logarithm of well depth</td>
<td>-2.0797</td>
<td>4.8282</td>
<td>0.028</td>
</tr>
<tr>
<td>Percentage total correct identifications: 81</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Model C: Probability of atrazine detection (logistic regression)

Model A was formulated using only data from area 1. The model predicted nitrate-nitrogen concentrations using specific conductance, the average hydraulic conductivity of the unsaturated zone, and the median completion date of irrigation wells within a 1-mi radius of the sampled well. Specific conductance is believed to be an indirect measure of nitrate-nitrogen concentration, as nitrate-nitrogen was one of the principal anions in many of the collected water samples. The average vertical hydraulic conductivity of the unsaturated zone demonstrated that increased permeability of the sediments enhanced the likelihood of ground-water contamination by nitrate-nitrogen. The median completion date of irrigation wells within a 1-mi radius showed that sites that had been under irrigation the longest had an increased probability of ground-water contamination by nitrate-nitrogen.

Model B was formulated using only data from area 1. The model predicted atrazine concentrations using nitrate-nitrogen concentration, depth to water, and the number of irrigated acres in a 1.7-mi radius of the sampled well and explained about 61 percent
Table 2. Results of comparisons of observed nitrate-nitrogen and atrazine concentrations from sites in Merrick County with predicted concentrations and probabilities of detection from selected models

<table>
<thead>
<tr>
<th>Observed nitrate-nitrogen concentration (mg/L)</th>
<th>Predicted nitrate-nitrogen concentration (mg/L)</th>
<th>Observed atrazine concentration (µg/L)</th>
<th>Predicted atrazine concentration (µg/L)</th>
<th>Probability of atrazine detection greater than 0.05 µg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>28</td>
<td>4.1</td>
<td>.60</td>
<td>.26</td>
<td>1.0</td>
</tr>
<tr>
<td>21</td>
<td>4.4</td>
<td>.30</td>
<td>.16</td>
<td>.95</td>
</tr>
<tr>
<td>16</td>
<td>18</td>
<td>Not analyzed</td>
<td>Not determined</td>
<td>Not determined</td>
</tr>
<tr>
<td>8.8</td>
<td>15</td>
<td>.50</td>
<td>.06</td>
<td>.84</td>
</tr>
<tr>
<td>18</td>
<td>15</td>
<td>.60</td>
<td>.13</td>
<td>.97</td>
</tr>
<tr>
<td>16</td>
<td>6.8</td>
<td>.60</td>
<td>.12</td>
<td>.90</td>
</tr>
<tr>
<td>21</td>
<td>12</td>
<td>1.4</td>
<td>.16</td>
<td>.97</td>
</tr>
<tr>
<td>4.3</td>
<td>7.2</td>
<td>.30</td>
<td>.04</td>
<td>.71</td>
</tr>
</tbody>
</table>

P-values from Wilcoxon rank sign test: 0.16

1. P-values greater than 0.05 are not significantly different at the 95-percent confidence level.

of the variation observed in atrazine concentrations. The presence of nitrate-nitrogen as an explanatory variable was not surprising given the overall correlation coefficient of 70 percent between nitrate-nitrogen and atrazine concentrations analyzed for this study. This supports the assumption that many of the factors affecting the transport of nitrate-nitrogen into the ground water also possibly affect the transport of atrazine. The depth-to-water variable demonstrates the greater likelihood of contamination with atrazine in areas with shallow water tables. The number of irrigated acres in a 1.7 mi radius of the sampled well is a measure of the intensity of irrigated agriculture and represents the effects of adjacent land use on water quality and the significance of lateral ground-water flow paths.

Model C was a logistic model using data from all study areas. The model predicted the probability of atrazine detections at or larger than the 0.01 µg/L detection limit using nitrate-nitrogen concentration, gradient of the potentiometric surface, percentage of clay in the soil, and the logarithm of well depth as explanatory variables. The presence of the potentiometric gradient in the model logically maintains that areas with flat gradients and relatively slow rates of ground-water flow may tend to accumulate atrazine at the water table faster than areas with relatively steep gradients. The percentage of clay represents the importance of soil permeability, and the log of well depth again demonstrates that deeper water supplies are not as easily contaminated by agricultural chemicals as shallow water supplies.

The overall effectiveness of the models was tested in two ways. First, water from eight irrigation wells in Merrick County (fig. 1), which is adjacent to area 1, was collected and analyzed for nitrate-nitrogen and atrazine concentrations independently of the data used to produce the models. Data quantifying the explanatory variables for each of the models were collected for each ground-water sampling site and predicted concentrations, or probabilities of detection, were compared to observed concentrations (table 2). The Wilcoxon rank sum test (Minitab, 1989), which compares population medians, showed
that the predicted nitrate-nitrogen concentrations were statistically similar to the observed concentrations at the 95-percent confidence level and that the atrazine concentrations predicted by model B were statistically smaller than observed atrazine concentrations. Model C predicted probabilities of atrazine detection of 0.71 to 1.0 for the seven irrigation wells for which atrazine data are available.

The second means of testing the models was through comparison of maps of observed and predicted ground-water concentrations of nitrate-nitrogen and atrazine (figs. 2-6). The predictive maps of nitrate-nitrogen and atrazine concentrations and probability of atrazine detection (figs 4-6) were selected to represent each of the explanatory variables in the models. The surfaces for each model were overlaid, and the predictive equations were solved using the explanatory variable values for each cell. The maps predicting nitrate-nitrogen and atrazine concentrations and probabilities of atrazine detection were compared to maps showing observed nitrate-nitrogen and atrazine concentrations generated from data sources other than those used to produce these models (Exner and Spalding, 1990).

In comparing the maps of observed and predicted concentrations, note that both the predicted nitrate-nitrogen and atrazine concentrations and the probability of atrazine detections look quite similar to the maps
of observed concentrations. Both maps of observed and predicted contamination show a generalized belt of ground-water contamination in the lowlands adjacent to the Platte River with some areas of larger concentrations superimposed on it. The upland areas north of the Platte River, where the depth to water is greater and where row-crop agriculture is less intense, show much smaller observed and predicted concentrations of nitrate-nitrogen and atrazine. Even in the upland areas, subtle effects, such as small stream drainages, are revealed by the predictive maps as being slightly more susceptible to ground-water contamination by agricultural chemicals than other upland areas. The fine detail shown on the predictive maps is the result of much larger data sets describing the explanatory variables (usually an order of magnitude larger) than the observed nitrate-nitrogen and atrazine data sets.

CONCLUSIONS

Multiple-regression and logistic regression techniques appear to be well suited for the generation of predictive ground-water-quality models. Although the models explained only 50 to 68 percent of the variation in nitrate-nitrogen and atrazine concentrations in ground water, the predicted concentrations and probabilities of detection generally agreed with observed contaminant concentrations from the eight wells in

Figure 3. Distribution of observed atrazine concentrations through 1989 in Buffalo and Hall Counties, south-central Nebraska.
Merrick County, and maps of predicted concentrations and probabilities of detection closely agreed with maps of observed concentrations of nitrate-nitrogen and atrazine in ground water in area 1.

The coupling of regression and logistic models that predict ground-water quality with a geographic information system, such as ARC/INFO, can be a powerful tool for evaluating models as they are generated and for utilizing the models after they have been completed. The modeling and graphic representation permits the user to define basic relations between selected ground-water contaminants and physical factors that may be affecting those concentrations and to use the relations to better define areas of potential ground-water contamination beyond the immediate areas of observed water-quality data sites. In fact, the explanatory variable data sets are commonly orders of magnitude larger than the dependent variables and can yield much larger coverages with finer detail than is possible with most contaminant data bases.
Figure 5. Distribution of predicted atrazine concentrations in ground-water in Buffalo and Hall Counties, south-central Nebraska.

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Figure 6. Distribution of probability of atrazine detection greater than or equal to 0.01 micrograms per liter in ground water in Buffalo and Hall Counties, south-central Nebraska.


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Comparison of Simulated and Observed Movement of Bank-Storage Water Adjacent to the Cedar River, Iowa

By Paul J. Squillace and David W. Pollock

Abstract

A ground-water flow model was constructed to describe quantitatively the movement of bank-storage water in an alluvial aquifer adjacent to the Cedar River, Iowa, during March 7-April 17, 1990, at the Palisades study area. The results from this two-dimensional model were compared to hydrologic and water-chemistry data. Hydrologic data consisted of 745 daily ground-water-level measurements made in 27 wells during March 8-April 5, 1990. These 745 measurements were used for model calibration and for comparing measured and simulated hydraulic heads and gradients. Water-chemistry data indicate that bank-storage water had a lower specific conductance and higher concentration of atrazine compared to the ambient ground water. Analysis of water chemistry and model results indicate that bank-storage water moved about 30 meters into the aquifer at a depth of 6 meters below land surface. The model also showed that 70 percent of the total bank-storage water moved through the river bottom while the remaining 30 percent moved laterally through the riverbank. The flux of bank storage-water both into and out of the river bottom is largest near the river's edge and decreases substantially with distance from the river's edge to the center of the river. The model showed that it would take about 5 weeks for bank-storage water to discharge from the alluvial aquifer after the peak river stage.

INTRODUCTION

During periods of snowmelt or rainfall, direct runoff to a river can cause an increase in river stage. Because of the increased river stage, river water can move through the river bottom and riverbank into the adjacent aquifer. As the stage declines, this same water is discharged back into the river. The volume of water so stored and released is referred to as bank storage. Bank storage attenuates the flood wave in a river with permeable bank materials (Pinder and Sauer, 1971) and can contribute substantial discharge to rivers during base flow (Kondolf, and others, 1987; Cooper and Rorabaugh, 1963; Squillace and others, 1993). Squillace and others (1993) have shown that atrazine is present in bank-storage water and that the discharge of this atrazine is probably the principal source of atrazine in the river during early base flow conditions. The movement of bank-storage water between surface water and ground water can be described analytically and by numerical flow models. Analytical solutions that describe and quantify the movement of bank-storage water between surface water and ground water have been presented by many researchers (Morel-Seytoux, 1975; Dever and Cleary, 1979; Hunt, 1990; Gill, 1985; Cooper and Rorabaugh, 1963; Moench and others, 1974; Newsom and Wilson, 1988); however, assumptions made for some of these calculations could be questionable and could yield erroneous values (Sharp, 1977). These assumptions include Dupuit-Forchheimer conditions, homogeneity, full penetration of streams, and systems that are solely confined or unconfined.

Numerical flow models can simulate the complex movement of bank-storage water in the alluvial aquifer; however, accurate simulation of this movement requires accurate and ample field data. The purpose of this paper is to (1) describe quantitatively the movement of bank-storage water at the Palisades

1U.S. Geological Survey, Rapid City, South Dakota
2U.S. Geological Survey, Reston, Virginia
study area adjacent to the Cedar River, Iowa, during March 8-April 17, 1990, by means of a ground-water-flow model, and (2) compare the model-simulation results with pertinent observed hydrologic and water-chemistry data. These water-chemistry data include specific conductance and the concentration of atrazine in ground water.

Acknowledgments

We would like to thank James Snyder for generously providing access to his land for the installation and monitoring of the observation wells.

DESCRIPTION OF STUDY AREA

The Palisades study area is located in an unfarmed flood plain of the Cedar River in east-central Iowa (fig. 1). The riverbank is approximately 4 m high at the water’s edge during low-flow conditions and slopes steeply down to the river (fig. 2). Nested monitoring wells were installed at selected distances from the river’s edge at the time of installation. As stage changes, the distance from the river’s edge to the wells also changes because the bank is not vertical. Therefore, the distance of the monitoring wells from the river edge depends on river stage and can be considered accurate to within several meters over the range of river stages simulated. The screened interval of each well is 75 cm and is positioned 3 to 9 m below land surface.

The Cedar River alluvium consists of a typical fluvial sequence of coarse-grained sand and gravel at the base that grades upward to fine-grained sand, silt, and clay at the surface. Test drilling at the study site showed that the alluvium is underlain by 15 m of till. The alluvium is 15 m thick but decreases in thickness with distance from the river. These unconsolidated sediments were subdivided into seven units on the basis of grain size and clay content. Slug tests performed at 24 observation wells showed a range of horizontal hydraulic conductivity from a high of 71 m/d in the coarse-grained alluvial sands to a low of 0.3 m/d in the clayey-silty units. Estimates of the hydraulic conductivity of the coarse-grained sand ranged from 25 to 80 m/d on the basis of aquifer diffusivity, which was calculated by comparing the response of the aquifer to fluctuations in the river stage by the method of Pinder and others (1969).

METHODS

The protocol for sampling the surface water and ground water is described by Squillace and others (1992). Atrazine was extracted from the water samples using solid-phase cartridges and then analyzed by gas chromatography/mass spectrometry according to the method of Thurman and others (1990).

RESULTS

Field Evidence for Bank Storage

In March 1990, direct runoff caused the river stage to increase almost 2 m and bank storage to occur because the normal ground-water hydraulic gradient, which was toward the river, was reversed. Hydraulic gradients were determined from 745 daily water-level measurements made during March 8-April 5, 1990, from both lines of wells along traces A-A’ and B-B’ shown in figure 1. Equipotential lines prepared from the water levels in the wells were parallel to the riverbank; therefore, the ground-water-flow paths during this time period were parallel to the two lines of wells shown in figure 1.

Bank storage of atrazine is demonstrated by water samples that were collected from wells and from beneath the river by means of a minipiezometer before, during, and after the March 1990, direct runoff event (fig. 2). Before direct runoff occurred, ground-water samples were collected during February 20-22, 1990. Analysis of these samples showed that background concentrations of atrazine in the aquifer ranged from 0.1 to 0.4 μg/L with one exception: a sample collected at the river’s edge at a depth of 1 m below land surface had an atrazine concentration of 0.66 μg/L. During direct runoff on March 20-22, 1990, the movement of bank-storage water into the aquifer was apparent because the concentrations of atrazine in the river increased to almost 1.0 μg/L when the river stage peaked on March 18, 1990, and these larger atrazine concentrations were carried into the aquifer with bank-storage water. Therefore, atrazine concentrations showed that bank-storage water moved 30 m into the aquifer at a depth of 6 m below land surface. After the direct runoff event, water samples were collected for analysis of atrazine concentration after the river returned to base-flow conditions during
April 3-5, 1990 (fig. 2). These results of these analysis show that large concentrations of atrazine were still present in the aquifer and that bank-storage water was still discharging to the Cedar River at that time. Squillace and others (1993) have shown that atrazine in this alluvial aquifer is in the dissolved phase and is not sorbed to the aquifer material in significant quantities.

Measurements of specific conductance shown in figure 3 confirm the movement of bank-storage water into the alluvial aquifer. The specific conductance in the river decreased from 840 μS/cm during February 20-22, 1990, to 580 μS/cm during March 20-22, 1990. Bank storage of river water caused the specific conductance in the alluvial aquifer to decrease in an area within 30 m of the river’s edge during March 20-22, 1990.
Simulation of Bank Storage

A two-dimensional ground-water-flow model was constructed using the U.S. Geological Survey's modular finite-difference ground-water flow model (McDonald and Harbaugh, 1988), with an option that allows model cells that have gone dry to become resaturated (McDonald and others, 1991). The model simulates ground-water flow in a two-dimensional cross section of the Palisades study area along the line of wells labeled A-A' (fig. 1 and 4), which is perpendicular to the Cedar River and is oriented parallel to the direction of ground-water flow. The cross-sectional area simulated in the model is 440 m wide and 15 m deep and is represented by a uniform grid with 15
layers, each with 44 cells (fig. 4). The depth of each cell in the plane of the cross-section is 1 m.

The river stage was simulated using a general head-dependent boundary (fig. 4), and the left lateral boundary beneath the center of the river was simulated as a no-flow boundary. The mean daily river stages at the Palisades site during March 7-April 12, 1990, was used for heads in the general head-dependent boundary. The river stage from April 13-17, 1990, increased slightly because of direct runoff. However, the river stage in the model was estimated by extrapolating the recession curve for another 5 days, so that the movement of bank storage out of the aquifer could continue for a longer time period. The left-lateral model boundary beneath the river (fig. 4) is assumed to be a ground-water divide.

The cells in contact with the river were also used to simulate the 0.5 m-thick streambed sediment along the riverbank and bottom (fig. 4). The presence of a thin layer of fine-grained streambed sediment along the riverbank has been documented in many rivers (Schumm, 1960) and may affect ground-water flow at the Palisades site.

The right-lateral model boundary farthest from the river (fig. 4) is assumed to be a no-flow boundary because of the presence of thick deposits (about 15 m) of glacial till in this area. The basal boundary is assumed to be a no-flow boundary because of the thick deposits (about 15 m) of glacial till that underlie the study area.

Recharge to the water table was treated differently in the steady state and transient simulations.
However, the steady-state model was used to generate the starting heads for the transient simulation. In the steady-state simulation, a constant uniform recharge was applied in columns 5-44. In the transient simulation, this same recharge was used in columns 5-43; however, in column 44, the recharge was increased to simulate an ephemeral stream. About 19 cm of precipitation fell during March 1990 and supplied direct runoff to this ephemeral stream. Measured vertical hydraulic gradients in the streambed indicate that this stream recharges the alluvial aquifer.

**Comparison of Model Simulation With Field Data**

The model was compared to field data as follows:

1. The largest horizontal hydraulic conductivities determined by the slug-test analysis and the flood-wave analysis were similar to those used in the model.

2. Daily ground-water-level measurements (a total of 745) made in 27 wells during March 8-April 5, 1990 were compared in three ways to calibrate the model. First, the mean difference between the measured and calculated heads for the wells located in columns 4-27 is 3.2 cm. Additional water levels measured in the wells shown in column 37 (fig. 4) were used to calibrate the model but were not compared to the model-generated heads. These measured water levels were excluded because they do not lie within the principal water-bearing unit of the aquifer and the water levels in the deepest well represented in column 37 were not at equilibrium because of sampling that occurred on March 20-22. Secondly, the vertical head differences from well nests at the Palisades site were compared to those in the model. The heads measured in the wells at 3 and 9 m depth correlate to heads in layers 4 and 10 of the model and are shown in figure 5. Thirdly, the horizontal ground-water hydraulic gradient between the wells 5 and 30 m from the riverbank were compared to the model-simulated hydraulic gradients in equivalent nodes.

3. Field data show that the area within 30 m of the river's edge contained bank storage water and was characterized by low specific conductance and a high concentration of atrazine when compared that in the background (or ambient) ground water (fig. 2 and 3).
This area also was identified as containing bank-storage water from preliminary analysis using a particle tracking post-processing package (D.W. Pollock, U. S. Geological Survey, written commun., 1993).

(4) Atrazine concentrations in samples collected during April 3-5, 1990 were used to estimate the areal extent of bank-storage water at that time. This area was also identified as containing bank-storage water based on a preliminary analysis using a particle tracking post-processing package (D.W. Pollock, U. S. Geological Survey, written commun., 1993).

(5) The current calibrated model does not explain the comparatively large concentrations of atrazine at 50 and 80 m from the river’s edge at a depth of 3 m below the land surface. Additional model runs are needed to determine whether the volume of bank storage could have expanded up to 80 m from the river’s edge.
During base-flow conditions, the amount of ground water that directly discharges to the Cedar River is comparable to the discharge calculated by the model. Along a 48-km reach of the Cedar River, the average ground-water discharge from the alluvial aquifer to the Cedar River was indirectly measured to be 2.1 and 1.8 m$^3$/d/m length of river, on two different occasions. The model calculated ground-water discharge to be 1.9 m$^3$/d/m length of river.

**Sensitivity Analysis**

Selected input parameters were varied from the calibrated values to determine the effects of variations in these parameters on model results. Table 1 shows the values that were changed in the sensitivity analysis. The range of values does not represent the absolute minimum and maximum values but are believed to include fairly extreme values.

The results of the sensitivity analysis show that the accumulation and release of bank-storage water is most sensitive to aquifer hydraulic conductivity, aquifer storage, and recharge. However, changes made in these parameters caused the heads to be significantly different from those calculated in the calibrated model and from field measurements. Changes in the other parameters did not cause the accumulation and release of bank-storage water calculated by the model to differ significantly from what was calculated by the calibrated model, even though the heads were somewhat different from those measured in the field. Increasing and decreasing the aquifer vertical anisotropy yielded calculated heads that were substantially different from those measured in the field. The hydraulic characteristics of the confining units do not substantially affect bank storage or the heads within the alluvial aquifer.

The vertical hydraulic conductivity of the 0.5-m-thick river bottom can be 50 percent less than the underlying aquifer and still not appreciably affect the movement of bank-storage water. Increasing the river-bottom hydraulic conductivity so that movement of river water into the aquifer is restricted only by the hydraulic conductivity of the aquifer resulted in little change in the accumulation and release of bank-storage water.

**Movement of Bank Storage Water in the Model**

The model showed that 70 percent of the total bank-storage water moved through the river bottom, whereas the remaining 30 percent moved laterally through the riverbank. More bank storage water moved through the river bottom because the river bottom has a surface area that is about 10 times larger than the surface area of the riverbank. However, per unit area, the flux of bank storage water through the riverbank was about 4 times as large as the flux through the river bottom because the horizontal hydraulic conductivities through the riverbank are larger than the vertical hydraulic conductivities through the river bottom.

The model showed that the flux of bank-storage water both into and out of the river bottom is largest near the river’s edge and decreases substantially with distance from the river’s edge to the center of the river. The flux through the river bottom reached a maximum on March 11, 1990. On this particular day, 48 percent of the flux through the river bottom occurred within 10 m of the river’s edge and 71 percent of the flux moved through the river bottom within 20 m of the river’s edge. The fluxes continued to decrease toward the center of the river.

Field measurements of the vertical and horizontal gradients of the alluvial aquifer under transient conditions were useful for calibrating the model. Model simulated hydraulic heads can closely match measured hydraulic heads, and yet still simulate the vertical movement of ground water erroneously. As an example, when the ground-water flux through the river bank is reduced to simulate streambed sediment the simulated hydraulic heads were similar to the measured heads. However, the vertical gradients in column 5 were reversed from those measured in the field at an equivalent location.

Bank storage is very sensitive to the recharge component; therefore, conceptually, the area of an alluvial aquifer that receives the smallest amount of recharge from precipitation and is located farthest from the effects of recharge in the upland areas has the greatest potential for bank storage and will retain the bank-storage water for the longest time, all other conditions being equal. Recharge from precipitation falling directly on the flood plain only supplies a small percentage of the ground water that discharges to the river.
Table 1. Calibrated values and range of values used in sensitivity analyses of the ground-water flow model

<table>
<thead>
<tr>
<th>Model input variable</th>
<th>Calibrated values</th>
<th>Range of values used in sensitivity analysis</th>
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<tr>
<td>Confining unit horizontal hydraulic conductivity (meters per day)</td>
<td></td>
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</tr>
<tr>
<td>glacial till</td>
<td>$1.0 \times 10^{-3}$</td>
<td>$1.0 \times 10^{-4}$</td>
</tr>
<tr>
<td>clay and silt</td>
<td>.01</td>
<td>.001</td>
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<td>silty clayey sand</td>
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<td>.1</td>
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<tr>
<td>Aquifer horizontal hydraulic conductivity (meters per day)</td>
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<td></td>
</tr>
<tr>
<td>silty sand</td>
<td>50.0</td>
<td>25.0</td>
</tr>
<tr>
<td>fine sand</td>
<td>1.0</td>
<td>0.5</td>
</tr>
<tr>
<td>medium sand</td>
<td>50.0</td>
<td>25.0</td>
</tr>
<tr>
<td>coarse sand</td>
<td>100.0</td>
<td>50.0</td>
</tr>
<tr>
<td>Confining unit vertical anisotropy</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Confining unit horizontal hydraulic conductivity/vertical hydraulic conductivity (meters per day)</td>
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<td></td>
</tr>
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<td>glacial till</td>
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<td>clay and silt</td>
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<tr>
<td>Aquifer vertical anisotropy</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aquifer horizontal hydraulic conductivity/vertical hydraulic conductivity (meters per day)</td>
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<td></td>
</tr>
<tr>
<td>fine sand</td>
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<td>medium sand</td>
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<tr>
<td>coarse sand</td>
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<td>2.0</td>
</tr>
<tr>
<td>silty sand</td>
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<td>2.0</td>
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<tr>
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<td>$.52 \times 10^{-3}$</td>
</tr>
<tr>
<td>stream-column 44</td>
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<tr>
<td>Specific yield--clean sand units</td>
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<td>.1</td>
</tr>
<tr>
<td>Specific yield--silty sand units</td>
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<td>.05</td>
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<tr>
<td>Specific storage</td>
<td>$1.0 \times 10^{-4}$</td>
<td>$1.0 \times 10^{-5}$</td>
</tr>
<tr>
<td>Confining unit storage (percent by volume)</td>
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<tr>
<td>Specific yield</td>
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<tr>
<td>Specific storage</td>
<td>$1.0 \times 10^{-3}$</td>
<td>$1.0 \times 10^{-4}$</td>
</tr>
<tr>
<td>River-bottom sediment</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Horizontal and vertical hydraulic conductivity (0.5-meter thick zone)(meters per day)</td>
<td>5.0</td>
<td>.5</td>
</tr>
<tr>
<td>River-bottom and bank sediment</td>
<td></td>
<td></td>
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<tr>
<td>Changed the horizontal and vertical hydraulic conductivity (0.5-meter thick zone) in the river bottom and riverbank at the same time.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>River bottom /riverbank (meters per day)</td>
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<td>200.0/0.5</td>
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533
The discharge of bank-storage water from the alluvial aquifer can continue for a long period of time. By extrapolation, the model showed that it would take about 5 weeks for bank-storage water to discharge from the alluvial aquifer at the Palisades study area after the river stage peaked on March 17, 1990.

REFERENCES


Abstract

In April 1991, a bromide tracer and the herbicides atrazine and alachlor were applied to a 0.75-hectare (ha) field plot of Eudora silt loam in the Kansas River Valley near Topeka, Kansas. The chemicals were immediately disked into the top 7.5 cm of soil, and the plot was planted with corn. Composite soil cores were collected from 12 contiguous cells in the plot, each 15 meters (m) by 15 m, at 15-centimeter (cm) depth intervals to 90 cm. Cores were collected immediately after application, then after 30, 60, and 120 days. Mean atrazine losses from the soil profile, relative to the immediate postapplication core results, were 75 percent at day 30, 92 percent at day 60, and 96 percent at day 120. Mean alachlor losses were 93 percent at day 30, 99 percent at day 60, and nearly 100 percent by day 120. The ratio of desethylatrazine metabolite to atrazine concentrations steadily increased in the top 15-cm soil layer during the 120-day period. An analysis of the soil-water budget and bromide distribution in the soil profile indicates that downward movement of the chemicals was restricted by a lack of significant downward soil-water flux during the growing season, when evapotranspiration was greatest. Loss of the herbicides from the soil profile is attributed mainly to degradation and transformation, and loss of bromide is attributed mainly to uptake by the crop. Low but persistent herbicide concentrations 120 days after application indicate that herbicide half lives are not constant and that herbicide residues could be tightly bound within solid-phase organic carbon and unavailable for biotic degradation.

INTRODUCTION

Agricultural herbicides are applied to soils throughout the world in increasing quantities for the control of weeds and grasses that would otherwise compete with crops. About 29 million kilograms of atrazine and about 25 million kilograms of alachlor are applied annually to soils in the United States, mainly in corn and soybean growing regions (Gianessi and Puffer, 1991). The ecological fate of these chemicals in soil is of interest to hydrologists, agriculturalists, and the public.

Agricultural herbicides are usually sprayed in liquid form just before spring planting, when soils are relatively moist and evapotranspiration rates are near minimum. Their fate is largely controlled by hydraulic properties of the soil and by weather conditions directly after application. When soil erosion is minimized and the herbicides are incorporated into shallow soil layers, the bulk of the chemicals will partition to organic material in the soil and will decay within the root zone as the crop matures. In some soils, however, especially under very wet spring conditions directly after application, soil water can flow relatively quickly in macropores through shallow soil zones and transport herbicide residues to deeper zones, thus minimizing residence time in zones of most active decay and increasing the potential for leaching into the ground water. Under dryer conditions, when soil-moisture content is less than field capacity and soil-water flow is commonly negligible, active herbicides are adsorbed and decay in shallow soil zones, where the organic-carbon content is generally the highest.
In 1991, the U.S. Geological Survey conducted a field study of alachlor and atrazine in unsaturated soils to document the spatial differences in chemical processes and transport rates that affect agricultural herbicides in soil. The study was intended to provide data to characterize the spatial and temporal variations in processes and rates in a numerical transport model of herbicide fate and movement within a 0.75-ha corn plot.

This paper describes the fate of atrazine and alachlor herbicides and a bromide tracer applied to the 0.75-ha silt-loam corn plot in Kansas during the 1991 growing season. It presents (1) results of analyses of soil cores taken throughout the plot at specified time and depth intervals after application and (2) describes results of preliminary model simulations of advective-dispersive solute movement that reflect the sorption and decay of herbicides in the unsaturated silt-loam.

METHODS

The field site is in the Kansas River Valley near Topeka, Kansas (fig. 1). The soil is a mesic profile with a 30-cm silt-loam A horizon (1 percent organic carbon (OC) over a silt-loam B horizon (0.4 percent OC). Depth to water table is about 6 m. Corn and soybean crops are rotated annually at the site. The 0.75 ha site consists of two adjacent rows of six 15-m by 15-m plots, each bounded by neutron-logging tubes for monitoring soil-water content.

In April 1991, alachlor (1.5 kg/ha active ingredient) and atrazine (1.5 kg/ha) herbicides and bromide tracer (70 kg/ha) were applied, and corn was planted. Soil cores were collected from six locations per plot cell and composited as one sample for each cell. Core samples were collected just before chemical application, immediately after application, and 30, 60, and 120 days thereafter in 15-cm lengths at depth intervals of 0 to 15 cm, 15 to 30 cm, 45 to 60 cm, and 75 to 90 cm. The soil samples representing the four depths in each of the 12 cells were split three ways, and each subsample was analyzed for gravimetric soil-moisture content, bromide content, and herbicide content. Bromide was extracted through a washing procedure with 0.005M CaSO₄ solution and analyzed by ion-chromatography. Herbicide residues in soil samples were analyzed by C-18 solid-phase extraction and gas chromatography with mass spectrometry, as described by Mills and Thurman (1992).

RESULTS AND DISCUSSION

The soil profile received 713 mm of water during 28 rainstorms and 7 spray irrigations during the modeled period of March through September 1991, which was slightly dryer than normal. Total evaporation from the profile (estimated to be 326 mm) occurred mainly in June, before the crop cover became significant. As the corn grew and roots penetrated deeper into the profile, transpiration (414 mm) became the main cause of water loss. Total estimated evapotranspiration (740 mm) during the 120-day growing season more than offset the rain and irrigation (713 mm) and slightly depleted available soil water in the profile. The net downward movement of water and chemicals was thereby minimized, and drainage loss by deep percolation was virtually zero.

Herbicide and tracer movement and fate were simulated by a one-dimensional numerical model (Wagenet and Hutson, 1992) that solves the Richards transient-state unsaturated flow equation and the advective-dispersive solute-transport equation with sorption, transformation, and root uptake by the growing crop. Soil-water movement was simulated from the hydraulic characteristics of soil as estimated through 20 onsite unit-gradient drainage experiments (Eckhardt and Barnes, 1991) and moisture-retention analysis of 160 soil cores collected from pits at the field site. The soil-water flow simulation was calibrated by adjusting evapotranspiration rates over time to reflect bromide distribution in soil cores and the changes in soil moisture content observed at 20 neutron-logging tubes that border each of the 12 core-sampling cells (fig. 1). Then, herbicide-transformation rates and sorption coefficients were adjusted to match observed herbicide mass balances and distributions in the soil profile over the 120-day growth period. Water and chemical movement and mass balances in an average soil profile 1 m thick were simulated. Growth of corn roots and the transpiration loss of water from the soil profile during the growing season were simulated with a root-growth model (Davidson and others, 1964) that represents water and chemical extraction from the soil profile as a function of root depth and density and time.
Bromide

Bromide, which had been applied to the plot just before planting, was used as a tracer to indicate average downward soil-water velocity during the growing season and the degree of hydrodynamic dispersion of solutes in the soil profile. Average downward soil-water velocity in the soil was less than 5 mm/d during the 120-day growing season; dispersivity was estimated to be 100 mm. During the 120 days after application, bromide was detected in all cores above the 30-cm depth, in 6 cores from the 60-cm depth, and in only 1 core from the 90-cm depth (1.4 mg/kg). The bromide distribution (fig. 2A) supports water-budget estimates that indicate that most of the water entering the soil as rain or irrigation was removed by evapotranspiration during the growing season and that drainage from the profile was minimal.

The mass of the applied bromide tracer was not conserved in the soil profile because dissolved...
Figure 2. The depth distribution of observed and simulated chemical concentrations in soil cores at three times after application in 1991: A. Bromide tracer, B. Alachlor, and C. Atrazine.
bromide was removed through uptake by the corn. At harvest in August 1991, less than 5 percent of the applied bromide remained in the soil. Analyses of corn grain and plant tissue indicate that more than half the applied bromide was taken up by the corn (table 1). Most of the bromide was concentrated in the stalks and leaves. The rest was probably in plant roots, which were not analyzed.

Bromide tracer in the simulated soil profile was lost mainly by crop uptake, which corresponded to root-growth and transpiration rates. Bromide mass in the simulated profile was relatively constant after application until about late June (60 days), when root development began to extract increased amounts of water and bromide from the rooting zone (fig 3). The discrepancy between low observed concentrations in soil cores 60 days after application and the higher simulated concentrations (fig. 2A) indicate that the root-growth model underpredicted the penetration and density of roots in the soil profile between days 30 and 60. An overprediction both in the soil-water content and bromide concentrations in the 15- to 30-cm layer on day 60 is further evidence that the roots at the field plot grew faster than the growth model predicted. Observed and simulated water contents at lower depths were in close agreement at all times.

**Herbicides**

Mean alachlor losses, relative to the immediate postapplication core results, were 93 percent at day 30, 99 percent at day 60, and nearly 100 percent by day 120. The partition coefficient (Koc) of alachlor was estimated to be 340 L/kg; therefore, its vertical movement in the soil profile was mainly within the top 15 cm (fig. 2B). Alachlor degraded relatively quickly within the first 60 days in the shallow soil profile (0 to 15 cm), where biological-decay activity is greatest and where alachlor readily partitions to the solid-phase organic carbon. During the first 60 days, the estimated half life of alachlor in the upper 15-cm soil layer was 11 days.

Mean atrazine losses from the soil profile, relative to the immediate postapplication core results, were 75 percent at day 30, 92 percent at day 60, and 96 percent at day 120. Atrazine moved slightly deeper in the soil profile (0 to 30 cm) than alachlor, because it is adsorbed less readily than alachlor (fig. 2C). The Koc of atrazine was estimated to be 170 L/kg, one-half that for alachlor. Atrazine degraded more slowly than alachlor and remained in the top 30 cm of soil at concentrations nearly twice those of alachlor. During the first 60 days, the estimated half life of atrazine in the upper 30-cm soil layer was 23 days.

The atrazine metabolite desethylatrazine (DEA) was formed in the soil through loss of the ethyl functional group by the bacterial action. DEA was not applied to the plot, nor was it detected in soil cores immediately after application. It reached its maximum concentration of about 3 μg/kg 30 to 60 days after application and was detected in nearly all samples from shallow soil layers (0-30 cm), where the atrazine was concentrated. The ratio of DEA to atrazine increased steadily after application for 60 days as DEA formed and atrazine was lost through hydrolysis and biodegradation (Adams and Thurman, 1991). A second atrazine metabolite, desisopropylatrazine, was detected infrequently at concentrations near the detection limit of 0.05 μg/kg.

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**Table 1. Bromide uptake by the corn crop after 120-day growing season, 1991**

<table>
<thead>
<tr>
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<th>STALK AND LEAVES</th>
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</tr>
<tr>
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<td>2,235</td>
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<table>
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<th>STALK AND LEAVES</th>
</tr>
</thead>
<tbody>
<tr>
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</tr>
<tr>
<td>B</td>
<td>1.7</td>
<td>41</td>
</tr>
<tr>
<td>C</td>
<td>1.7</td>
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<tr>
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<tr>
<td>MEAN</td>
<td>1.65</td>
<td>36</td>
</tr>
</tbody>
</table>
Alachlor and atrazine in the simulated soil profile were lost mainly through degradation in shallow soil layers during the first 60 days (fig. 3), when biological activity was greatest and herbicide residue was sufficient for bacterial activity. After 60 days, however, herbicide half lives apparently increased as herbicide concentrations decreased, and herbicide residues in soil cores remained, although at relatively low concentrations, 120 days after application (fig. 2). Residues of alachlor were detected 120 days after application in 75 percent of the cores from above 30-cm depths (maximum 10 μg/kg); residues of atrazine were detected in all samples from above 30-cm depths (maximum 16 μg/kg). These low but persistent concentrations indicate that the herbicide residues could be tightly bound within solid-phase organic carbon and unavailable for bacterial degradation. The uptake of herbicides by the growing
crop is estimated to be negligible because herbicides were largely degraded or partitioned to the solid phase by the time of significant root development.

SUMMARY AND CONCLUSIONS

In April 1991, bromide tracer and the herbicides atrazine and alachlor were applied to a 0.75-ha field plot of Eudora silt loam in the Kansas River Valley near Topeka, Kansas. The chemicals were immediately disked into the top 7.5 cm of soil, and the plot was planted with corn. Composite soil cores were collected from 12 contiguous cells in the plot, each 15 m by 15 m, at 15-cm intervals to the 90-cm depth.

Movement and fate of the herbicide and tracer were simulated with a one-dimensional numerical model that solves the Richards equation of unsaturated transient-state flow and the advective-dispersive solute-transport equation that describes sorption, transformation, and root uptake by the growing crop. An analysis of the soil-water budget and bromide distribution in the soil profile indicates that downward movement of the chemicals was restricted by a lack of significant downward soil-water flux during the growing season, when evapotranspiration was greatest. Most of the water that entered the profile as rain or irrigation was lost through evapotranspiration during the 120-day growing season; drainage loss by deep percolation was close to zero.

Bromide tracer mass was not conserved in the soil profile because dissolved bromide was removed from the soil through uptake by the corn. At harvest in August 1991, less than 5 percent of the applied bromide remained in the soil. Results of bromide analysis of corn grain and plant tissue show that more than half of the applied bromide was taken up by the corn crop, and the balance of 45 percent of the bromide is assumed to have been in the roots, which were not analyzed.

Alachlor degraded relatively quickly within the first 60 days after application and remained mostly in the shallow soil profile (0 to 15 cm), where bacterial activity is greatest and where alachlor readily partitions to the solid-phase organic carbon. The estimated alachlor half life in the upper 15 cm through the first 60 days after application was 11 days. Atrazine moved slightly deeper (0 to 30 cm) than alachlor because it partitions less readily than alachlor, and it degraded less quickly; its estimated half life in the upper 30 cm through the first 60 days after application was 23 days. After 60 days, herbicide half lives apparently increased as herbicide concentrations decreased, and herbicide residues remained at relatively low concentrations 120 days after application. The low but persistent residue concentrations indicate that the herbicides could be tightly bound within solid-phase organic carbon and unavailable for bacterial degradation.

REFERENCES


By Matthew K. Landon¹, Geoffrey N. Delin¹, John A. Lamb², Robert H. Dowdy³, and James L. Anderson²

Abstract

The 65-hectare Management Systems Evaluation Area (MSEA) near Princeton, Minnesota is one of five primary MSEA's in the Midwest Cornbelt. The Princeton MSEA program is a cooperative research effort among the U.S. Department of Agriculture-Agricultural Research Service, the University of Minnesota Soil Science Department, and the U.S. Geological Survey. The primary program objective is to evaluate the effects of ridge-tillage practices in corn and soybean farming systems on ground-water quality in a sandplain setting. A sweet-corn and potato farming system is also being evaluated. Analyses of samples collected at the beginning of the study during April 1991 indicated that some contamination of ground water with nitrate nitrogen (nitrate-N), atrazine, and atrazine metabolites had already occurred before implementation of the MSEA farming systems.

Chloride in potash fertilizers applied to the MSEA cropped areas in April 1991 was used as a tracer for ground water affected by the MSEA farming systems. Chloride reached ground water beneath all of the cropped areas. Analyses of ground-water samples collected during June, August, and December 1991 and during April 1992 indicated that concentrations of chloride in the upper meter of the saturated zone beneath and downgradient of the cropped areas were 20 to 50 mg/L (milligrams per liter) compared with background concentrations of 2 to 19 mg/L.

Because the nitrogen and potash fertilizer application rates on the potato-cropped area were 1.4 and 4.5 times greater, respectively, than on the other cropped areas, nitrate-N and chloride concentrations were greatest beneath the potato-cropped area. Nitrate-N concentrations in the upper meter of the saturated zone beneath the potato-cropped area (22-47 mg/L) were greater than concentrations measured upgradient (6-18 mg/L) from the cropped area. Nitrate-N concentrations were similar upgradient, beneath, and downgradient of the other cropped areas. Thus, additions of nitrate-N as a result of MSEA activity were difficult to distinguish from background concentrations. Concentrations of nitrate-N in the saturated zone across the entire MSEA typically decreased from 15 to 25 mg/L near the water table to 5 to 10 mg/L two meters below the water table.

Atrazine and atrazine metabolites de-ethylatrazine (DEA) and de-isopropylatrazine (DIA) were detected in 75, 97, and 76 percent, respectively, of the 124 wells sampled at the Princeton MSEA during the four sampling periods from June 1991 through April 1992. The concentrations of these compounds in the saturated zone varied temporally. Atrazine was detected in 51 percent of the 315 ground-water samples collected in concentrations ranging from less than 0.01 μg/L (micrograms per liter) to 0.54 μg/L. The median concentration of atrazine was the detection limit of 0.01 μg/L. DEA was detected in 74 percent of the samples at concentrations ranging from less than 0.03 μg/L to 1.00 μg/L. The median concentration of DEA was 0.08 μg/L. DIA was detected in 10 percent of the samples in concentrations ranging-

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³U.S. Department of Agriculture, Agricultural Research Service, St. Paul, Minn.
from less than 0.06 μg/L to 0.66 μg/L. The median concentration of DIA was less than the detection limit of 0.06 μg/L. Alachlor was detected in 2 percent of the samples. Concentrations of DEA in April 1992 increased with depth from less than 0.06 μg/L near the water table to 0.08 to 0.30 μg/L between 1 and 2 m below the water table. This trend with depth was not noticeable prior to April 1992 and could indicate that water recharging the aquifer beneath the cropped areas during 1991 had lower DEA concentrations than older ground water.

Because some of the applied fertilizers and herbicides and herbicide metabolites existed in shallow ground water at the onset of this study, it is difficult to assess the affects of MSEA farming systems on water quality without additional data collected over several years. None of the detections of herbicides or herbicide metabolites can be conclusively linked to the MSEA farming systems at this time. Because some atrazine and atrazine metabolites were detected in ground water that was recharged through the MSEA cropped areas, however, the possibility that some of these chemicals leached from the MSEA farming systems to ground water cannot be discounted. Use of conservative tracers like chloride and bromide to delineate annual recharge fronts beneath the MSEA cropped areas should make it easier to identify the affects of MSEA farming systems on ground-water quality as older ground water affected by previous farming practices moves horizontally and vertically away from the cropped areas.

INTRODUCTION

The northern cornbelt sand-plains Management Systems Evaluation Area (MSEA) program is a multistate initiative to evaluate the effects of farming systems on ground-water quality in a sandplain area in Minnesota and at satellite areas in North and South Dakota, and Wisconsin (Delin and others, 1992a). The primary objective of this program is to evaluate the effects of ridge-tillage practices in a corn and soybean farming system on ground-water quality. The Minnesota MSEA is located in the Anoka Sand Plain near the town of Princeton (fig. 1). The Princeton MSEA program is a cooperative study primarily between the U.S. Department of Agriculture-Agricultural Research Service, the University of Minnesota Soil Science Department, and the U.S. Geological Survey. The Minnesota Pollution Control Agency and the Department of Geology at the University of Minnesota are also cooperating in the evaluation of ground-water quality at the MSEA. This paper describes the effects of farming systems on ground-water quality at the Princeton MSEA during the first year of implementation (1991).

DESCRIPTION OF THE PRINCETON, MINNESOTA MSEA

Topographic relief at the 65-ha area is less than 3 m. Mostly, the unsaturated zone consists of fine-to-medium-grained sand and the saturated zone consists of medium-to-coarse grained sand. The unsaturated and saturated zones contain discontinuous layers of silt and very-fine-grained sand up to 20 cm thick. A clayey till underlies the surficial aquifer (the till is less permeable than the aquifer). During 1991, the average depth to the water table was about 3.6 m below land surface, and the saturated thickness ranged from 4 to 16 m across the study area. The average horizontal saturated hydraulic conductivity is about 0.04 cm/s. Ground water generally moves from west to east (fig. 1) at an average rate of about 8 cm/d. The method of hydrograph analysis of Rasmussen and Andreason (1959) was used to calculate ground-water-recharge rates. Recharge generally ranged from 10 to 20 cm in the study area during 1991.

In 1991, five 1.8- to 2.6-ha cropped areas were aligned parallel to the predominant direction of ground-water flow at the study site (fig. 1). These areas were used to evaluate three cropping systems (Anderson and others, 1991): (1) a corn-soybean annual rotation under ridge (conservation) tillage, split nitrogen (N) application, N credit for legumes, and banding of herbicides (application only over row and amounting to one-third of the broadcast application amount) (fig. 1, field corn and soybeans); (2) a sweet corn-potato annual rotation with conventional full-width (disk or chisel) tillage, banding of herbicides for sweet corn, and broadcast application of herbicides for potatoes (fig. 1, sweet corn and potatoes); and (3) field corn in consecutive years (continuous corn) under conventional full-width tillage and broadcast application of herbicides (fig. 1, continuous corn). Application rates of agricultural chemicals in 1991 are shown in table 1.
EXPLANATION

- **Potatoes**: Cropped area and 1991 crop type
- **Irrigation well**: Data point, number indicates chloride concentration, in milligrams per liter
- **Continuous Corn**: Observation well, number indicates number of wells at site
- **Field Corn**: Multiport well
- **Sweet Corn**: Building
- **Soybeans**: Approximate line of equal chloride concentration, interval in 10 milligrams per liter
- **Potatoes**: Cropped area, including cropped areas
- **Direction of ground-water flow, January, 1991**: The research area is located in the northeast quarter of section 18, township T35N, range R26W.
- **Line of section A—A’**: Figure 1. Layout of the Princeton, Minnesota, Management Systems Evaluation Area and example illustrating contouring of chloride concentrations along a cross section beneath the potato-cropped area, April 1992.
Table 1. Application rates of agricultural chemicals on crops at the Princeton, Minnesota, Management Systems Evaluation area, 1991
[All application rates are broadcast rates; band, application of herbicide only over row, amount is one-third of the total amount per hectare for broadcast application. kg/ha, kilograms per hectare; --, not applied]

<table>
<thead>
<tr>
<th>Agricultural chemical</th>
<th>Potatoes</th>
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<th>Sweet corn</th>
<th>Field corn</th>
<th>Continuous corn</th>
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<tr>
<td></td>
<td>Total rate kg/ha</td>
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<td>Total rate kg/ha</td>
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<td>April</td>
<td>112</td>
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<tr>
<td>Nitrogen</td>
<td>224</td>
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<td>--</td>
<td>--</td>
<td>157</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Herbicide</td>
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<tr>
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<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
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</tr>
<tr>
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<td>Metolachlor</td>
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<td>May</td>
<td>--</td>
<td>--</td>
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</table>

A buffer area around and between the cropped areas (fig. 1) was planted with a mixture of timothy and smooth brome grass. Agricultural chemicals were not applied in this buffer area. The entire 65-ha field was planted in alfalfa during 1981-89 and in corn during 1990, prior to the implementation of the MSEA farming systems in spring 1991. Detailed records of farming practices and chemical applications during this period were not available.

The ground-water-quality sampling network at the Princeton MSEA consists of 29 observation wells and 22 multiport wells (fig. 1). In addition, 14 observation wells are located off the 65-ha field (not shown in fig. 1). Observation wells were used to measure water levels monthly and to determine background concentrations of agricultural chemicals. These wells are constructed of 5.1-cm inside-diameter (i.d.) galvanized-steel or polyvinyl chloride (PVC) casing with 0.6-m-long screens located at the water table or 0.15-m-long screens installed deeper in the aquifer. The multiport wells are located 21 m upgradient, in the middle, at the downgradient edge, and 25 m downgradient (slightly less than the distance ground water travels in 1 year) of each cropped area (fig. 1). Each multiport well consists of six, 0.6-cm i.d. stainless-steel tubes housed in a 5.1-cm i.d. PVC casing; each tube has a 3-cm-long screened interval (port) which is external to the PVC casing. The sampling ports were installed at 0.5-m intervals with the uppermost port 0.5 m above the water table to allow sample collection if the water table rose.

Water samples were collected during 1991 at four different times from all multiport wells, selected onsite observation wells, and Battle Brook (fig. 1). These samples were collected before the application of agricultural chemicals (April), twice during the growing season (June and August), and in the late fall after crops were harvested (December). Sample-collection and laboratory-analysis quality-assurance/quality-control protocols were followed (MSEA Steering Committee, written commun., 1991). Specific conductance, pH, temperature, dissolved oxygen concentration, and oxidation-reduction potential of ground water were measured during pumping at each sampling site.
Water samples were collected once these properties stabilized. Alkalinity titrations were performed the same day in the field. Water samples were collected and analyzed for dissolved major cations and anions, nutrients, and selected herbicides and herbicide metabolites (atrazine, de-ethylatrazine (DEA), de-isopropylatrazine (DIA), alachlor, chloroalachlor, 2,6-diethylanaline, metolachlor, and metribuzin). Gas chromatography/mass spectrometry was used to determine herbicide concentrations (P.D. Capel, U.S. Geological Survey, written commun., 1991).

GROUND-WATER QUALITY, 1991

Concentrations of selected water-quality constituents in the upper 2 m of the saturated zone were contoured along a cross section extending beneath each MSEA cropped area (figs. 1-4). The contouring is somewhat speculative because of the wide horizontal spacing of the data points. Contour intervals were selected that best emphasized contrasts in constituent concentrations along each cross section.

Because potash (potassium chloride) fertilizer was applied only to the cropped areas (fig. 1 and table 1) and because chloride moves conservatively with ground water, chloride was used as a tracer of water recharged through the cropped areas. Where concentrations of chloride and nitrate nitrogen (nitrate-N) were clearly greater beneath a cropped area than upgradient, contours were drawn to reflect the interpretation that the source of the higher concentrations was recharge of chemicals from the overlying cropped area. For example, beneath the potato cropped area during April 1992 (fig. 1), the 20-mg/L chloride contour was extended to the upgradient (west) end of this area because the source of the higher chloride concentrations was considered to be downward movement of chloride to ground water from the cropped area.

Most of the closed contours in figures 1-4 are artifacts of the contour intervals selected. The closed contour around the 32.3-mg/L chloride concentration in figure 1, for example, likely represents a volume of water that was recharged through the overlying potato-cropped area. This volume of water could have become isolated within water that had lower chloride concentrations because of temporal variations in fluxes of water and chemicals to the saturated zone. Other closed contours in figures 1-4, particularly for the herbicides, likely represent mixing of waters in the aquifer and are not related to the MSEA farming systems. For atrazine and DEA, the contour intervals chosen were the reporting and detection limits for each compound. Because there is uncertainty associated with the reproducibility of these herbicide analyses near their detection limits, there is also uncertainty associated with the locations of the herbicide-concentration contour lines (figs. 2, 3, and 4).

Chloride.—Chloride concentrations (23-26 mg/L) greater than background (2-19 mg/L) were first detected in the upper 1 m of the saturated zone beneath the field corn-cropped area (fig. 2) during the June 1991 sampling period, about 1.5 months after application. Chloride concentrations (33-37 mg/L) greater than background were first detected in the upper 1 m of the saturated zone beneath the potato- (fig. 3) and soybean-cropped areas during the August 1991 sampling period, about 4 months after application. Chloride concentrations (21-31 mg/L) greater than background were first detected in the upper 1 m of the saturated zone beneath the potato-cropped area during the December 1991 sampling period, about 7.5 months after application. On the basis of these times of first detection of elevated chloride concentrations, the estimated time of travel of water and chloride moving through the unsaturated zone was 1 to 7.5 months. These traveltimes are maximum values because the sampling periods were not frequent enough to identify first arrival of the chloride tracer. In addition, relatively high background concentrations (2-19 mg/L) of chloride partially conceal increases in chloride concentrations that could have resulted from recharge through the MSEA cropped areas. These traveltimes are comparable with a traveltime of 75 days determined in a dye-tracing study done during 1991 (Delin and others, 1992b).

The April 1992 data reflect the affects of agricultural practices in 1991 and earlier on ground-water quality because agricultural chemicals had not yet been applied for the 1992 growing season. Additional inputs of chloride and continued spread of chloride through the aquifer occurred during spring 1992 (figs. 2-4) when approximately 6.4 cm of recharge occurred. Chloride concentrations were greatest beneath the potato-cropped area (fig. 4), reflecting that the chloride (potash fertilizer) application on the potato-cropped area was 4.5 times greater than that used with any other crop (table 1). Chloride concentrations in April 1992 in the upper 1 m of the saturated zone beneath the cropped areas ranged from 20 to 50 mg/L compared with concentrations of 2 to 19 mg/L away from the cropped area.
Figure 2. Chloride, nitrate nitrogen, atrazine, and de-ethylatrazine concentrations along a cross section beneath the field-corn cropped area during the June 1991 through April 1992 sampling periods at the Princeton, Minnesota, Management Systems Evaluation Area.
Figure 3. Chloride, nitrate nitrogen, atrazine, and de-ethylatrazine concentrations along a cross section beneath the potato-cropped area during the June 1991 through April 1992 sampling periods at the Princeton, Minnesota, Management Systems Evaluation Area.
Figure 4. Chloride, nitrate nitrogen, atrazine, and de-ethylatrazine concentrations along a cross section beneath cropped areas at the Princeton, Minnesota, Management Systems Evaluation Area, during the April 1992 sampling period.
areas and deeper than 1 m in the saturated zone. These results indicate that shallow ground-water quality reflects recent (May 1991 to April 1992) ground-water recharge. This conclusion is supported by chloride concentrations near the water table beneath the buffer areas (less than 10 mg/L) that were less than concentrations deeper in the saturated zone (10-20 mg/L) or beneath the MSEA cropped areas (fig. 2, 3, and 4). Because chloride was not applied in these buffer areas during 1991, ground water near the water table beneath these areas likely was recharged during 1991. Ground water with chloride concentrations of 10 to 20 mg/L 1 to 2 m below the water table beneath the entire MSEA probably represent ground water unaffected by farming systems implemented for the MSEA study.

Nitrate-nitrogen.—Ground-water samples were collected from 14 observation wells within the 65-ha MSEA during April 1991 before the implementation of the MSEA farming systems. Seven of the 14 wells were located within the area that was cropped before 1991. Concentrations of nitrate-N in these 7 wells ranged from 2 to 23 mg/L; the median concentration was 10 mg/L.

Nitrate-N concentrations (22-47 mg/L) greater than those measured upgradient and 1 to 2 m below the water table (6-18 mg/L) were first detected at the water table beneath the potato-cropped area (fig. 3) during the December 1991 sampling period, about 7.5 months after application. Nitrate-N concentrations increased beneath the potato-cropped area by April 1992 compared to earlier sampling periods (fig. 3). Nitrate-N concentrations were greatest beneath the potato-cropped area (fig. 4), reflecting an application rate on the potato-cropped area that was 1.4 times greater than on any other cropped area (table 1). Because nitrate-N concentrations were similar upgradient, beneath, and downgradient of the other cropped areas, additions of nitrate to ground water as a result of the MSEA farming systems research could not be clearly distinguished from background concentrations (figs. 2 and 4).

Elevated concentrations of nitrate-N (greater than 20 mg/L) were measured near the water table beneath the field corn-cropped area in June 1991 and the sweet corn-cropped area in April 1992 (figs. 2 and 4). These nitrate-N concentrations were greater than typical background concentrations (0.1-18 mg/L) and were within the part of the saturated zone affected by recharge through the MSEA cropped areas, as delineated by the chloride data (figs. 2 and 4). However, these nitrate-N concentrations did not exceed the highest background nitrate concentrations of 25 mg/L. Therefore, it cannot be concluded at this time whether the elevated nitrate-N concentrations beneath the sweet corn and field corn were due to inputs from the MSEA farming systems or were background concentrations.

Nitrate-N concentrations in the saturated zone across the entire MSEA typically decreased from 15 to 25 mg/L near the water table to 5 to 10 mg/L 2 m below the water table. Similarly, dissolved oxygen concentrations typically decreased from near saturation with the atmosphere (from greater than 8 parts per million (ppm)) at the water table to less than 3 ppm 2 m below the water table. This decrease in dissolved-oxygen concentrations with depth implies that oxygen was being consumed by biochemical oxidation-reduction reactions faster than it could be replenished by advection of oxygen-rich water from the water table (Ronen and others, 1987; Champ and others, 1979). Concentrations of nitrate-N were less than 0.2 mg/L 7 m below the water table, where the water was generally anoxic, indicating that the decrease in nitrate-N concentrations continued between 2 and 7 m below the water table. This decline in nitrate-N concentrations could indicate that nitrate-N was denitrified at depth within the aquifer (Postma and others, 1991; Trudell and others, 1986).

Because nitrogen fertilizer was not applied to the buffer areas, the nitrate-N (15 to 25 mg/L at the water table) beneath the buffer areas during 1991 likely resulted from the residual effects of previous land use. Possible sources of nitrate-N reaching the ground water include decomposition of alfalfa roots and residues in the soil (from cropping with alfalfa during 1981-1989) or application of nitrogen fertilizer to the corn grown during 1990.

Herbicides.—During April 1991, before implementation of the MSEA farming systems, atrazine, DEA, and DIA, were detected in 2, 9, and 3, respectively, of the 14 observation wells sampled within the 65-ha MSEA. The median concentrations for atrazine, DEA, and DIA were less than 0.01, 0.10, and less than 0.01 μg/L, respectively, and maximum concentrations were 0.17, 2.30, and 0.98 μg/L respectively. No samples had concentrations of atrazine that exceeded the U.S. Environmental Protection Agency (1986) advisory level of 3 μg/L.

Atrazine, DEA, and DIA were detected in 75, 97, and 76 percent, respectively, of the 124 wells sampled at the Princeton MSEA during the four sampling periods from June 1991 through April 1992. The
Table 2. Concentrations of herbicides and herbicide metabolites in 315 ground-water samples collected during four sampling periods from June 1991 through April 1992 at the Princeton, Minnesota, Management Systems Evaluation area, 1991

[DEA, de-ethylatrazine; DIA, de-isopropylatrazine; µg/L, micrograms per liter; <, less than; >, greater than. Number (#) of detections greater than the reporting limit or detection limit]

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<th>Atrazine µg/L</th>
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<th>DIA µg/L</th>
<th>Alachlor µg/L</th>
<th>2,6-Diethyl-analine µg/L</th>
<th>Chlor-alachlor µg/L</th>
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<tr>
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>Detection limit<sup>1</sup>

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</table>

<sup>1</sup> The quantitative reporting limit for atrazine, DEA, DIA, alachlor, 2,6-diethylanaline, chloralachlor, metolachlor, and metribuzin analyses were 0.04, 0.06, 0.08, 0.04, 0.04, 0.08, 0.04, and 0.06 µg/L, respectively. The qualitative detection limit for atrazine, DEA, DIA, alachlor, 2,6-diethylanaline, chloralachlor, metolachlor, and metribuzin analyses were 0.01, 0.03, 0.06, 0.01, 0.01, 0.06, 0.01, and 0.03 µg/L, respectively.

Concentrations of these compounds in the saturated zone varied both spatially and temporally. Summary statistics for herbicide and herbicide metabolite concentrations in 315 samples collected during these sampling periods are shown in table 2. Detections of atrazine (from less than 0.01 to 0.54 µg/L, median 0.01 µg/L), DEA (from less than 0.03 to 1.00 µg/L, median 0.08 µg/L), and DIA (from less than 0.06 to 0.66 µg/L, median less than 0.06 µg/L) (table 2) beneath the buffer areas and beneath the cropped areas where atrazine was not applied (the potatoes, figs. 3 and 4, and soybeans, fig. 4) indicate that background concentrations of these compounds were present that were unrelated to the MSEA farming systems. DEA was the most frequently detected herbicide or herbicide metabolite and had the greatest median concentration. Concentrations of DEA in April 1992 increased with depth from less than 0.06 µg/L near the water table to 0.08 to 0.30 µg/L between 1 and 2 m below the water table. This trend with depth was not noticeable prior to April 1992 and could indicate that water recharging the aquifer beneath the cropped areas during 1991 had lower DEA concentrations than older ground water. There were few clear spatial or temporal trends in the distribution of other herbicides or metabolites in the ground water from June 1991 through April 1992.

Atrazine in low concentrations (0.01-0.47 µg/L) was detected within the region of the saturated zone affected by recharge through the sweet corn-, field corn-, and continuous corn-cropped areas as delineated using the chloride data (figs. 2 and 4). Because similar atrazine concentrations were detected in ground water...
recharged beneath areas where atrazine was not applied, these detections cannot be currently linked to the MSEA farming systems. However, the possibility still exists that some of the atrazine used in the MSEA farming systems may reach ground water. Additional data over a multi-year period will be needed to evaluate whether atrazine applied as part of the MSEA farming systems reaches ground water. Possible sources for the widespread background concentrations of atrazine and atrazine metabolites at the MSEA are application of atrazine to the field corn grown on the 65-ha MSEA during 1990, one year prior to implementation of the MSEA, or application before 1980 (prior to cropping with alfalfa).

Alachlor and its metabolites chloroalachlor and 2,6-diethylanaline were infrequently detected in low concentrations at the MSEA (table 2). These compounds were detected both beneath cropped areas where alachlor was applied and in areas where it was not applied, indicating that there were background levels of these compounds. There were no detections of metolachlor or metribuzin beneath cropped areas where these chemicals were applied.

**DISCUSSION AND SUMMARY**

The total mass of chloride and nitrogen applied to the MSEA cropped areas that reached the saturated zone was estimated. Concentrations of chloride and nitrate-N in the upper 1 m of the saturated zone beneath the cropped areas that exceeded background concentrations were assumed to have resulted from leaching of chemicals applied to the cropped areas. The concentrations in excess of background concentrations were multiplied by the estimated volume of aquifer affected to estimate the mass of chemicals in the saturated zone derived from the MSEA farming systems. The total mass of MSEA-derived chloride in the upper 2 m of the saturated zone beneath the potato-cropped area (120 kg/ha) exceeded the mass beneath each of the other cropped areas (60 kg/ha) because 4.5 times more chloride was applied on the potato-cropped area than on the other cropped areas. About 32 percent of the chloride applied to the potato-cropped area and 71 percent of the chloride applied to the other cropped areas during April 1991 likely reached the saturated zone by April 1992. The percentage of applied chloride that reached the saturated zone beneath the potato-cropped area likely was less than for the other cropped areas because the flux of water that moved through the unsaturated zone was insufficient to transport more of the applied chloride to the water table. The residual chloride could indicate that carryover of chemical applications occurred from one growing season to the next. Residual chloride is likely to continue to leach from the unsaturated zone during subsequent recharge events. About 21 percent of the nitrogen applied to the potato-cropped area during April and June 1991 reached the saturated zone by April 1992. Because the inputs of nitrate-N from the other MSEA cropped areas could not be distinguished from background concentrations, the percentage of applied nitrogen that reached the saturated zone could not be determined beneath these other cropped areas.

Use of chloride in potash fertilizers applied to the cropped areas as a tracer for water recharged through these areas allowed delineation of a region of the saturated zone affected by the MSEA farming systems. With the exception of comparatively high nitrate-N concentrations beneath the potato-cropped area concentrations of nitrate-N, herbicides, and herbicide metabolites within this region of the saturated zone were generally similar to background concentrations. This indicates that the effects of the MSEA farming systems on ground-water quality were no greater than the effects from previous cropping practices. The background concentrations of chloride, nitrate-N, herbicides, and herbicide metabolites, however, make it difficult to evaluate fully the effects of MSEA farming systems on ground-water quality without additional data over several years. Use of conservative tracers, such as chloride and bromide, to delineate annual recharge fronts beneath the cropped areas should make it easier to describe the effects of MSEA farming systems on ground-water quality as older ground water, affected by previous farming practices, moves horizontally and vertically away from the cropped areas.

**REFERENCES**


Effects of Topography on the Transport of Agricultural Chemicals near Princeton, Minnesota, 1992

By Geoffrey N. Delin and Matthew K. Landon

Abstract

In 1991, the U.S. Geological Survey (USGS), with funding from the USGS Toxic Substances Hydrology Program, began studying the movement of water and agricultural chemicals at the Management Systems Evaluation Area (MSEA) near Princeton, Minnesota. The research is being conducted in a topographically low (lowland) site and a topographically high (upland) site within the northernmost cropped area at the 65-hectare Princeton MSEA. The sites are about 78 m (meters) apart and with a difference in land-surface elevation of 1.4 meters. Soils in the upper meter at both the upland and lowland sites are similar and are composed of about 95 percent sand and 5 percent silt and clay. The grain size is coarser between the 1.0- and 2.0-m depths at the lowland site than at the upland site, however. Total organic carbon in the upper 20 cm of topsoil is about 1.0 percent at the lowland site and about 0.6 percent at the upland site. Water sampling and monitoring equipment were installed at the upland and lowland sites following a dye-tracing and trenching study that was conducted to identify zones of preferential and retarded water movement and to collect soil samples from the unsaturated zone.

Infiltration tests were conducted during 1992 at the upland and lowland sites following selected precipitation events or by the application of 2.5 cm of water from a linear-move sprinkler irrigation system. The movement of wetting fronts through the unsaturated zone to the water table were evaluated using time-domain reflectometry. Water samples were collected from suction lysimeters as the wetting front passed a given lysimeter elevation, and from water-table wedges after the wetting front reached the saturated zone.

Wetting fronts typically penetrated deeper into the unsaturated zone at the lowland site than at the upland site during 1992. In addition, the total flux of water into the soil at the lowland site was greater than at the upland site. Following application of about 8 cm of water beginning June 29, 1992, for example, recharge through the unsaturated zone was about 1.0 cm at the lowland site compared to about 0.5 cm at the upland site, based on hydrograph analysis. For this recharge event, the estimated fluxes of nitrate nitrogen and atrazine through the unsaturated zone to the water table at the lowland site were 3.5 and 5 times greater, respectively, than the fluxes at the upland site. Differences in the movement of wetting fronts, agricultural chemicals, and tracers at the upland and lowland sites likely resulted from a combination of factors including differences in soil organic matter, grain size, porosity, sedimentary heterogeneities, antecedent moisture conditions, and topographic relief. Possible mechanisms that could cause focused recharge of water and agricultural chemicals at the lowland site include surface runoff and iron-rich layers that form a barrier to vertical water movement through the unsaturated zone at the upland site.

INTRODUCTION

Previous studies have indicated that greater ground-water recharge occurs in topographically low (lowland) areas compared to topographically high (upland) areas (Meyboom, 1966; Lissev, 1968). This increased flux of ground-water recharge in lowland areas has been termed focused recharge. The effects of
agricultural activities on ground-water quality have been investigated in numerous field studies at various scales. These range from regional studies covering thousands of square kilometers (Helgesen and others, 1991; Burkart and others, 1991) to plot-scale studies of the effects of macropores, tillage, and crop rotation (Kanwar, 1991; Cameron and others, 1979). Little is known, however, about the effects of focused recharge on the concentrations and fluxes of agricultural chemicals in lowland areas. An improved understanding is needed of how topography and focused recharge affect the movement of agricultural chemicals. In 1991, the U.S. Geological Survey (USGS), with funding from the USGS Toxic Substances Hydrology Program, began a study of the movement of water and agricultural chemicals to the water table at the Management Systems Evaluation Area (MSEA) near Princeton, Minnesota (fig. 1).

The primary objective of this 4-year research study is to evaluate the effects of transient recharge, topography, and subsurface heterogeneities on the flux of water and agricultural chemicals to the water table. The approach used was to (1) install instruments to sample and measure the movement of water through the unsaturated zone beneath upland and lowland sites of a corn field at the Princeton, Minnesota MSEA; (2) conduct recharge and tracer tests in the field to evaluate the movement of water and agricultural chemicals at both topographic settings; and (3) simulate the field recharge and tracer tests in the laboratory (Delin and Landon, 1993). The purpose of this paper is to describe preliminary results of ongoing research on the effects of topography on water and chemical movement at the Princeton MSEA. Data from 1992 are presented, that describe differences in the movement of water and selected agricultural chemicals as related to topography.

DESCRIPTION OF RESEARCH SITES

The research is being conducted at an upland site and a lowland site within the northernmost area cropped in corn at the 65-ha Princeton MSEA (fig. 1). The upland and lowland sites are about 78 m apart and differ in land-surface elevation by 1.4 m (slope of about 0.02). The unsaturated zone mostly is a fine- to medium-grained sand and the saturated zone mostly is a medium- to coarse-grained sand (Delin and others, 1992a). The soils in the upper meter at both the upland and lowland sites are similar and are composed of about 95 percent sand and 5 percent silt and clay. The grain size is coarser, however, between the 1.0- and 2.0-m depths at the lowland site than at the upland site. Total organic carbon in the upper 20 cm of topsoil is about 1.0 percent at the lowland site and about 0.6 percent at the upland site (J.A. Lamb, University of Minnesota Soil Science Department, written commn. 1993).

During October 1991, the water table was about 4 m below land surface at the upland site and 2.8 m below land surface at the lowland site. The mean saturated horizontal hydraulic conductivity in the upper meter of the unsaturated zone at both sites was similar (about 3.6x10^{-3} cm/s, (H.W. Olsen, U.S. Geological Survey, written commun., 1993)). Below the 1-m depth at the lowland site, where the grain size is coarser, the mean saturated horizontal hydraulic conductivity (1.9x10^{-3} cm/s) is greater than that for the same depth interval at the upland site (4.8x10^{-3} cm/s). On the basis of water-level hydrograph analyses, ground-water recharge rates were 10 to 20 cm per year at the Princeton MSEA and ground-water-flow gradients were 0.0009 to 0.002 during 1991. Ground-water flow is from southwest to northeast beneath the upland and lowland sites at a velocity that varies seasonally from 6 to 15 cm per day. Ground-water-flow directions, however, shift to a more northerly direction as a result of focused recharge in lowland areas (fig. 1).

The herbicides atrazine and alachlor were applied to the research sites during May 1991 and May 1992 at broadcast rates of 1.7 and 2.25 kg/ha active ingredients, respectively. Nitrogen fertilizer was applied during April to June 1991 and during June 1992 at rates of 157 kg/ha and 123 kg/ha, respectively. Potash fertilizer was applied during April 1991 and during May 1992 at rates of 112 kg/ha and 45 kg/ha, respectively. Chloride in the potash fertilizer has been used as a tracer of water recharging through the MSEA cropped areas (Landon and others, 1993). The entire 65-ha field was planted in alfalfa from 1981 to 1989, prior to the implementation of the MSEA farming systems in spring 1991. Detailed records of farming practices and chemical applications during this period were not available.

METHOD OF STUDY

Before the unsaturated-zone instruments were installed, a dye-tracing and trenching study was done at the upland and lowland sites to identify zones of preferential and retarded water movement and to characterize the unsaturated-zone properties (Delin and others, 1992b). A 3-percent solution of rhodamine
Planimetric View of Instrument Locations at the Upland and Lowland Sites

- Vertical profile of nine time-domain-reflectometry probes, nine thermocouples, and five tensiometers
- Vertical profile of three suction lysimeters
- Multiport well
- Precipitation gage
- Water-table well
- Trench
- Dye-application area

EXPLANATION

- Boundary of cropped area
- Lowland areas
- Topographic contour. Shows altitude of land surface. Interval 0.25 meters. Datum is sea level.
- Observation well, number indicates number of wells at site.
- Multiport well

The research area is located in the northeast quarter of section 18, township T35N, range R26W.

Figure 1. Instrument locations at the upland and lowland sites, land-surface topography, and lowland areas at the Princeton, Minnesota, Management Systems Evaluation area (MSEA).
WT dye was applied uniformly as a tracer to a 3.5-m by 6-m area at each site (fig. 1). About 12 L of dye was applied at 10-day intervals from July 5 through September 13, 1991 to ensure complete penetration of the unsaturated zone. Total rainfall from July 5 through October 22, 1991 was about 30 cm. Beginning October 22, 1991, a 3-m by 2-m trench was dug in the middle of each dye-application area. The depth of each trench was increased by intervals of 0.5-m to a total depth of 2.0 m to locate the dye and to collect soil samples from the unsaturated zone. Delin and others (this volume) provide a detailed description of the dye-tracing and trenching study.

The following instruments were installed in two vertical profiles at the upland and lowland sites (fig. 1) on the basis of the presence or absence of dye: (1) thermocouples and time-domain reflectometry (TDR) probes, at depths of 0.2, 0.4, 0.6, 0.8, 1.0, 1.5, 2.0, 2.5, and 3.0 m; (2) suction lysimeters, at depths of 0.8, 1.8, and 2.8 m; and (3) tensiometers, at depths of 0.5, 1.0, 1.5, 2.0, and 2.5 m. TDR is a technique in which electronic pulses are transmitted through a coaxial cable that is attached to a fixed-length probe embedded in the soil (Topp and others, 1980). The resultant waveform is affected by the moisture content of the soil surrounding the probe. Because the dielectric constant of water is much higher than that of most other materials, a signal in moist soil will propagate more slowly than in the same soil when dry. Thus, the moisture content can be calculated by measuring the waveform propagation time over the fixed-length probe. TDR-measured moisture contents at the lowland site correlated well (R²=0.92) with neutron-probe measurements (M.D. Tomer, University of Minnesota, Soil Science Department, written commun., 1992).

A water-table well was installed upgradient of each trench so that concentrations of agricultural chemicals reaching the water table could be determined (fig. 1). Soil temperature, soil moisture, soil-water tension, ground-water levels, and precipitation were continuously recorded at both sites with data loggers.

Infiltration tests were conducted during 1992 at the upland and lowland sites following selected precipitation events or by the application of 2.5 cm of water from a linear-move sprinkler irrigation system. The movement of wetting fronts through the unsaturated zone to the water table were evaluated using TDR. Water samples were collected from the suction lysimeters and the water-table wells before each infiltration test to determine pre-test concentrations of the agricultural chemicals. Samples were also collected of the irrigation water or precipitation. Following the application of irrigation water, water samples were collected from the suction lysimeters as the wetting front passed a given lysimeter elevation, and from the water-table well after the wetting front reached the water table.

The water samples were analyzed for dissolved major anions (including nitrate-nitrogen (nitrate-N), chloride, sulfate, and bromide) using ion chromatography and analyzed for selected herbicides and herbicide metabolites (atrazine, de-ethylatrazine (DEA), de-isopropylatrazine (DIA), alachlor, chloroalachlor, 2,6-diethylalanine, metolachlor, and metribuzin) using gas chromatography/mass spectroscopy (P.D. Capel, U.S. Geological Survey, written commun., 1991). In addition to the water sampling, soil samples were collected by the University of Minnesota Soil Science Department from the upland and lowland sites six times per year. The soil samples were analyzed for concentrations of nitrate-N and the herbicides atrazine, alachlor, and metolachlor (MSEA Steering Committee, written commun., 1991).

### WATER INFILTRATION AT THE UPLAND AND LOWLAND SITES

The movement of wetting fronts was different at the upland and lowland sites during 1992. Wetting fronts typically penetrated deeper into the unsaturated zone at the lowland site than at the upland site. About 24 hours after 2.5 cm of irrigation water was applied on June 9, for example, the wetting front at the upland site had moved to a depth of only 0.8 m below land surface (fig. 2). By comparison, the wetting front at the lowland site reached the water table (about 2.8 m below land surface) after the same 24-hour period resulting in ground-water recharge and a water-level rise of about 0.3 cm. The increase in moisture content from the 2.0-m depth to the 2.5-m depth at the lowland site (fig. 2) is because the TDR probe at the 2.5-m depth was located within the capillary fringe. The decrease in moisture content at the lowland site from June 10 to June 11 from the 0.8-m depth to the 2.0-m depth at the lowland site (fig. 2) was due to drainage of water from the unsaturated zone as a result of recharge to the saturated zone. The increase in the amount of water stored in the soil from June 9 to June 10 at the lowland site (3.7 cm) was greater than the amount stored in the soil at the upland site (2.3 cm). Focused recharge occurred
at the lowland site because the amount of water stored in the unsaturated zone (3.7 cm) was greater than the amount of water applied (2.5 cm). Additional evidence of focused recharge is that the water table rose at the lowland site in response to the irrigation but did not rise at the upland site.

During a recharge event beginning June 29, 1992 about 8 cm of water (irrigation and rainfall) was applied to the upland and lowland sites over a 4-day period. Measurements of daily precipitation and irrigation, profiles of volumetric moisture content, and water-level fluctuations for the lowland site from June 29 through July 8, 1992 are shown in figure 3. Continuous measurements of volumetric moisture content were not measured at the upland site. The water applied during the first 3 days of the recharge event brought the soil moisture to field capacity. Field capacity is defined as the amount of water remaining in a soil 2 or 3 days after having been wetted and after free drainage is negligible (Cassel and Nielsen, 1986). The field capacity is different for each soil depth and at the 1.0-m depth, for example, corresponds to a volumetric moisture content of about 0.10 (fig. 3). The 4-cm of rainfall that occurred on July 2 caused the soil moisture to exceed the field capacity, resulting in the wetting front moving through the 2.8-m-thick unsaturated zone beneath the lowland site in about 4 days (93 hours). In response to this recharge, the water-table rose about 2 cm over a 3-day period at the lowland site compared to only about a 0.6-cm rise at the upland site. On the basis of this water-table response and a specific yield of 0.3, recharge through the unsaturated zone at the lowland site for this event was about 1.0 cm, compared to about 0.5 cm at the upland site. These results indicate that even when recharge occurred in both topographic settings, greater recharge occurred at the lowland site.

The apparent pattern of soil-water movement as indicated by rhodamine-WT distributions in the unsaturated zone did not reflect measured soil-water distributions during 1992. Soil-water movement in what was identified as a retarded flow zone during the dye-tracing study actually moved faster, not slower, than the soil-water movement identified as a preferential flow zone. This difference indicates that the zones of preferential flow observed on the trench walls did not extend greater than about 10 cm beyond the face of the trench or failed to encompass the entire length of the installed TDR probes. In addition, it is likely that the probes installed in what was considered a preferential flow zone might actually have penetrated an adjacent zone of retarded flow.

Differences in the movement of wetting fronts at the upland and lowland sites could have resulted from a combination of factors that include differences in organic content, grain size, porosity, sedimentary heterogeneities, antecedent moisture conditions, evapotranspiration, and topographic relief. Delin and others (this volume) provide a description of the differences in unsaturated-zone properties at the upland and lowland sites.

One mechanism that could cause focused recharge to occur at the lowland site is surface runoff. Runoff was observed at the Princeton MSEA during periods of intense or prolonged rainfall such as the one that began on June 29, 1992, when about 8 cm of irrigation water and rainfall were applied to the upland and lowland sites (fig. 3). Runoff was never observed, however, during recharge events such as the one that began June 9, 1992, during which only about 2.5 cm of irrigation water was applied to each site during a 1-hour period (fig. 2). Thus, mechanisms other than runoff must be contributing to focused recharge at the research site during periods of limited water application.
Figure 3. Daily precipitation and irrigation, profiles of volumetric moisture content, and water-table fluctuations for the lowland site at the Princeton, Minnesota, Management Systems Evaluation area, June 29-July 8, 1992.
Table 1: Concentrations of agricultural chemicals at the upland and lowland sites at the Princeton, Minnesota Management Systems Evaluation Area, 1992
[ATR, atrazine; DEA, de-ethylatrazine; DIA, de-isopropylatrazine; mg/L, milligrams per liter; μg/L, micrograms per liter; #, number; <, less than; --, no samples analyzed]

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<td>1.4</td>
<td>.04</td>
<td>.08</td>
<td>&lt;.06</td>
</tr>
<tr>
<td>Median</td>
<td>21.1</td>
<td>15.1</td>
<td>0.08</td>
<td>0.21</td>
<td>0.15</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Water table</th>
<th>Nitrate-nitrogen, mg/L</th>
<th>Chloride, mg/L</th>
<th>ATR, μg/L</th>
<th>DEA, μg/L</th>
<th>DIA, μg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td># of analyses</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Maximum</td>
<td>15.9</td>
<td>25.3</td>
<td>0.03</td>
<td>0.14</td>
<td>0.10</td>
</tr>
<tr>
<td>Minimum</td>
<td>12.5</td>
<td>15.9</td>
<td>&lt;.01</td>
<td>&lt;.03</td>
<td>&lt;.06</td>
</tr>
<tr>
<td>Median</td>
<td>13.5</td>
<td>19.8</td>
<td>.02</td>
<td>.04</td>
<td>&lt;.06</td>
</tr>
</tbody>
</table>

1. The qualitative detection limit for atrazine, de-ethylatrazine, and de-isopropylatrazine analyses were 0.01, 0.03, and 0.06 μg/L, respectively. The quantitative reporting limit for atrazine, de-ethylatrazine, de-isopropylatrazine analyses were 0.04, 0.06, and 0.08 μg/L, respectively.

The presence of iron-rich layers in the unsaturated zone at the upland site could also be a factor contributing to focused recharge at the lowland site. The 2 to 20 cm thick layers are cemented with iron oxides, and contain an average of about 5 to 10 percent silt and clay, compared to less than about 5 percent in adjacent horizons. The layers were detected in soil cores and observed in the trench walls at the upland site, primarily between the 1- and 2-m depth intervals, and extend to below side-slope areas (M.D. Tomer, University of Minnesota, Soil Science Department, oral commun., 1993). The layers were not observed in the trench walls at the lowland site. Because of the iron-oxide cement and the higher percentage of silt- and clay-sized particles compared to the surrounding soil, the layers form barriers that could retard the vertical flow of water through the unsaturated zone. Thus, the iron-rich layers likely retain water, and agricultural chemicals, that would otherwise penetrate deeper than this depth into the unsaturated zone at the upland site. The net effect likely is a reduction in the flux of water and agricultural chemicals through the unsaturated zone beneath the upland site. Some of the water and agricultural chemicals retained in the iron-rich layers could be used by plants, further reducing the fluxes to the water table. Another possible effect of the iron-rich layers terminating beneath the side-slope areas is that water could move horizontally along these layers toward the lowland site over short distances of perhaps 1 to 2 m. The net effect of this horizontal movement along numerous iron-rich layers could be increased soil-water movement to the lowland site.

WATER QUALITY AT THE UPLAND AND LOWLAND SITES

Concentrations of nitrate-N in water samples in the unsaturated zone at the lowland site were greater than those in the unsaturated zone at the upland site during 1992 (table 1, above). Nitrate-N concentrations in the unsaturated zone were generally greatest during April of 1992 at both sites, immediately following the application of agricultural chemicals, but changed little throughout the summer and fall. Concentrations of nitrate-N from the water table at the lowland site were slightly greater than concentrations from the upland site (table 1). By comparison, median concentrations of nitrate-N in soil samples collected during 1991 from
the 0-to 0.8-m depth interval at both the upland and lowland sites were 3.2 mg/kg J.A. Lamb, University of Minnesota, Soil Science Department, written commun., 1993).

Concentrations of chloride in water samples in the unsaturated zone at the lowland site were less than those in the unsaturated zone at the upland site during 1992 (table 1). As with nitrate-N, chloride concentrations in the unsaturated zone were greatest during April of 1992 at both sites, immediately following the application of agricultural chemicals, but changed little throughout the summer and fall. Concentrations of chloride were similar in water samples from the water table at the upland and lowland sites during 1992 (table 1).

Concentrations of atrazine in water samples collected from the unsaturated zone at the lowland site were slightly greater than concentrations at the upland site during 1992 (table 1). Concentrations of DEA and DIA from the unsaturated zone at the upland site were slightly greater than at the lowland site. The concentrations of atrazine, DEA, and DIA in samples from the water table were below or near the qualitative detection limits at both sites (table 1). As with data from the water analyses, the median concentration of atrazine in soil cores collected during 1991 from the 0- to 0.5-m depth interval at the lowland site (19.5 ng/g) was slightly greater than the median at the upland site (13.0 ng/g) J.A. Lamb, University of Minnesota, Soil Science Department, written commun., 1993). Atrazine was not detected above the detection limit of 5 ng/g in soil samples below the 0.6-m depth from either site during 1991.

The concentrations of nitrate-N, chloride, atrazine, DEA, and DIA (table 1) were within the range of background concentrations at the MSEA (Landon and others, this volume). Because increased recharge at the lowland site should have caused the concentrations of agricultural chemicals to be diluted, however, it was expected that the concentrations would be lower at the lowland site than at the upland site. This hypothesis is supported by data from the unsaturated zone for chloride, DEA, and DIA, as well as by data from the water table for chloride and DEA (table 1). The concentrations of nitrate-N and atrazine, however, were greater at the lowland site than at the upland site in both the unsaturated zone and at the water table. The greater concentrations of nitrate-N and atrazine at the lowland site could have resulted from a concentrating of the chemicals due to runoff and along flow paths through the unsaturated zone. The greater atrazine concentrations at the lowland site could have also resulted from greater biodegradation at the upland site because of a longer residence time in the unsaturated zone compared to the lowland site.

The fluxes of nitrate-N, chloride, atrazine, DEA, and DIA through the unsaturated zone to the water table were estimated for the recharge event beginning June 29, 1993 (table 2). The calculated water fluxes for this recharge event of 0.5 and 1.0 cm/d were used for the upland and lowland sites, respectively. Median concentrations of the agricultural chemicals for unsaturated-zone samples collected during 1992 were used (table 1) in this analysis because water samples were not available for this recharge event. The median concentrations shown in table 1 are representative of the climate and farming practices during the growing season. The estimated fluxes for all of the agricultural chemicals, except DEA, were greater at the lowland site than at the upland site (table 2). The differences were greatest for nitrate-N and atrazine where the estimated fluxes at the lowland site were 3.5 and 5 times greater, respectively, than corresponding fluxes at the upland site. The greater fluxes at the lowland site are mostly the result of increased recharge rather than higher chemical concentrations.

The fact that atrazine and its metabolites were detected in water samples collected from most depths in the unsaturated zone and from the water table at the upland and lowland sites indicates that some of the applied herbicide moved through the unsaturated zone to the water table as a result of farming practices at the MSEA. Atrazine was not detected, however, in soil samples below the 0.6-m depth, primarily because the detection limit for atrazine in soil samples of 5 ng/g is too large to detect the lower concentrations of any herbicides present. The 5-ng/g detection limit for soil analyses corresponds to aqueous concentrations of 5 μg/L. These results indicate that full evaluation of the movement of atrazine to the water table requires analyses of water samples from the unsaturated zone in addition to analyses of soil samples.

The limited number of chemical analyses from the upland and lowland sites during 1992 (table 1) limits the conclusions that can be made from these preliminary results. Additional analyses are needed to make definitive statements about differences in the concentrations and fluxes of agricultural chemicals at the upland and lowland sites.
Table 2. Estimated fluxes of water and agricultural chemicals to the water table at the upland and lowland sites for the June 29 through July 9, 1992 recharge event at the Princeton, Minnesota Management Systems Evaluation area

<table>
<thead>
<tr>
<th></th>
<th>Upland site</th>
<th>Lowland site</th>
<th>Lowland flux divided by upland flux</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water flux, cm/d</td>
<td>0.5</td>
<td>1.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Nitrate-nitrogen flux, (kg/d)/ha</td>
<td>3.52</td>
<td>12.4</td>
<td>3.5</td>
</tr>
<tr>
<td>Chloride flux, (kg/d)/ha</td>
<td>2.52</td>
<td>3.93</td>
<td>1.6</td>
</tr>
<tr>
<td>Atrazine flux, (kg/d)/ha</td>
<td>1.33x10^-5</td>
<td>6.67x10^-5</td>
<td>5.0</td>
</tr>
<tr>
<td>De-ethylatrazine flux, (kg/d)/ha</td>
<td>3.5x10^-5</td>
<td>2.0x10^-5</td>
<td>0.6</td>
</tr>
<tr>
<td>De-isopropylatrazine flux, (kg/d)/ha</td>
<td>2.5x10^-5</td>
<td>3.0x10^-5</td>
<td>1.2</td>
</tr>
</tbody>
</table>

CONCLUSIONS

Results of this study indicate that even small land-surface differences of only 1.4 m over a 78-m horizontal distance (slope of about 0.02) can result in focused recharge in lowland areas. Possible mechanisms that could cause focused recharge of water containing agricultural chemicals at the lowland site include surface runoff and iron-rich layers that form a partial barrier to vertical water movement through the unsaturated zone at the upland site. Based on analyses of few samples collected during 1992, the fluxes of most agricultural chemicals to the water table were greater at the lowland site than at the upland site, primarily because of increased recharge at the lowland site compared to the upland site. Additional analyses are needed to make definitive statements about the differences in the concentrations and fluxes of agricultural chemicals at the upland and lowland sites.

REFERENCES


Spatial Variability of Unsaturated-Zone Properties in Relation to Topography in a Sand-Plain Setting near Princeton, Minnesota

By G.N. Delin¹, M.K. Landon¹, R.W. Healy², and H.W. Olsen³

Abstract

The spatial distribution of preferential flow paths and unsaturated-zone properties in two topographic settings were determined from a dye-tracing and trenching study done at the Management Systems Evaluation Area (MSEA) near Princeton, Minnesota. The topographic settings are upland and lowland sites about 78 m (meters) apart that differ in elevation by 1.4 m. A 3 percent solution of rhodamine-WT dye was applied uniformly as a tracer to a 3.5- by 6-m area at both sites at 10-day intervals from July 5 through September 13, 1991. After application of the dye, a 3- by 2-m trench was dug to a depth of 2 m in the middle of each dye-application area to locate the dye and to collect soil samples.

Water samples were collected periodically from a multiport well, located 2.5 m horizontally downgradient of each dye-application area, to estimate the time-of-travel of recharge water through the unsaturated zone. The dye was first detected in ground water about 100 days after application. On the basis of average ground-water velocity at the Princeton MSEA of 10 cm/d (centimeters per day), the transport velocity of dye through the unsaturated zone was calculated to be 3.7 cm/d at the lowland site and 5.3 cm/d at the upland site. The dye moved 2 m vertically through the saturated zone over a horizontal distance of about 9 m, whereas a steady-state ground-water-flow model predicted less than 0.2 m of vertical movement.

A total of about 450 soil samples were collected from the sides and bottom of the trenches for analyses of bulk density, dye fluorescence, grain-size distribution, hydraulic conductivity, moisture-retention characteristics, organic-carbon content, and volumetric moisture content. The distribution of dye through the unsaturated zone was highly variable at the upland and lowland sites. Dye movement was greatest beneath the furrows and least beneath the corn rows. Preliminary results indicate the dye moved preferentially in response to tillage patterns (corn rows and furrows), microtopography, presence of plant roots, differences in total organic carbon, and coarser-grained heterogeneities in the unsaturated zone. Visible dye distribution did not correlate strongly with bulk density, saturated hydraulic conductivity, moisture-retention characteristics, and volumetric moisture content.

INTRODUCTION

Two factors that affect water movement through the unsaturated zone are spatial variability of soil properties (Delhomme, 1979; Sharma and others, 1980; and Russo and Bresler, 1981) and topography (Meyboom, 1966). Spatial variability of soil properties affects the pathways and rates of water movement. Among the important soil properties that can affect water movement are bulk density, grain-size distribution, hydraulic conductivity, moisture-retention characteristics, organic-carbon content, and volumetric moisture content. This study was designed to evaluate the effects of spatial variability of these soil properties on the distribution of preferential flow paths in upland and lowland areas in sandy soils.

This paper describes preliminary results of ongoing studies by the U.S. Geological Survey of unsaturated-zone properties at the Management Systems Evaluation Area (MSEA) near Princeton, Minn. (fig. 1).

¹U.S. Geological Survey, Mounds View, Minn.
Figure 1. Layout of the Princeton, Minnesota, Management Systems Evaluation Area.
Preliminary results of a dye-tracing and trenching study are presented. The study is being done at a topographically high (upland) site and a topographically low (lowland) site within the northernmost cropped area at the 65 ha Princeton MSEA (fig. 1). The upland and lowland sites are about 78 m apart and differ in elevation by 1.4 m (slope of about 0.02). During October 1991, the water table was about 4 m below land surface at the upland site and 2.8 m below land surface at the lowland site. On the basis of well hydrograph analyses, ground-water discharge rates range from 10 to 20 cm/y at the Princeton MSEA (Delin and others, 1992a). Ground-water-flow gradients ranged from 0.0009 to 0.002 during 1991. Ground-water flow is from southwest to northeast beneath the upland and lowland sites at a velocity that varies seasonally between 6 and 15 cm/d.

METHODOLOGY

Instruments used to make measurements in the unsaturated-zone can be installed either vertically in a borehole or horizontally in a trench wall. Horizontal installation in a trench wall is preferred to minimize disturbance of the unsaturated zone above the instruments, and to facilitate identification of lateral heterogeneities in soil properties. Heterogeneities in soil properties can produce preferential flow paths along which water and solutes move more rapidly than through the soil matrix. Most gross heterogeneities can be identified visually within a trench, such as a gopher burrow filled with coarse sand in silty soil. Other heterogeneities, such as subtle differences in grain size, are commonly difficult to visually identify. Instruments installed in a soil heterogeneity can yield data that are not representative of typical unsaturated flow for the site.

A dye-tracing and trenching study was done at the upland and lowland sites to (1) identify zones of preferential and retarded water movement, (2) facilitate collection of soil samples to characterize unsaturated-zone properties, (3) select installation sites for unsaturated-zone instruments, and (4) estimate the transport velocity of water and solutes moving through the unsaturated and saturated zones (Delin and others, 1992b). Rhodamine WT dye was used in this study because it has been used successfully as a tracer of water and agricultural chemicals moving through sandy soils similar to the Princeton MSEA (Omoti and Wild, 1979; Trudgill, 1987; and Kung, 1990). Results of the Kung (1990) study indicated that the dye adsorbs to the soil matrix, allowing for tracing of dominant paths of water movement in the unsaturated zone. The dye has also been used as a tracer of ground water in the saturated zone of alluvial sand aquifers (Sabatini and Austin, 1991).

A 3 percent solution by volume of the dye was applied uniformly to a 3.5 by 6 m area at each site (fig. 1). About 12 L of dye was applied at 10-day

![Figure 2](image-url)  
**Figure 2.** Cumulative precipitation and concentration of dye in ground water 1.0 meter below the water table and 2.5 meters downgradient of the dye-application area at the lowland site, Princeton, Minn., 1991.
intervals from July 5 through September 13, 1991 (fig. 2) to ensure dye visibility and complete penetration through the unsaturated zone. Dye was also applied near several aluminum neutron access tubes installed at each site. Total rainfall from July 5 through October 22, 1991, was about 30 cm (fig. 2).

Beginning on October 22, 1991, a 3- by 2-m trench was dug in the middle of each dye-application area. The depth of each trench was increased by intervals of 0.5 m to a total depth of 2.0 m. The long walls of each trench coincided with a corn row. Photographs of the sides and bottom of each trench were taken to document the visible distribution of dye in the unsaturated zone. Following dye application, water samples were collected periodically from a multiport well located 2.5 m horizontally downgradient of each dye-application area (fig. 1). Each multiport well consisted of six 0.6-cm diameter stainless-steel tubes housed in a 5.1-cm inside diameter (i.d.) polyvinyl chloride (PVC) casing; each stainless-steel tube had a 3-cm-long screened interval (port) which was external to the PVC casing. Five sampling ports were installed below the water table at 0.5 m intervals. Water samples were collected periodically from each port and analyzed for dye concentration to estimate the transport time of water and solutes moving through the unsaturated zone.

Soil samples, 20 cm³ in volume, were collected from the sides and bottom of each trench for measurements of grain-size distribution, bulk density, total organic-carbon content, volumetric moisture content, and dye fluorescence. About half of the samples were located beneath the corn rows and half beneath the furrows. About 25 samples were collected at regularly spaced intervals of about 1.0 m horizontally and 0.5 m vertically from the northern and eastern walls of each trench. About 25 and 60 samples were collected at irregular spacing to facilitate geostatistical analysis of the data from the southern and western walls of each trench, respectively. About 20 samples were collected at regularly spaced intervals from the bottom of each 0.5-m depth interval in the trench to determine the three-dimensional distribution of dye. Fourteen soil samples were collected adjacent to and 0.05 m away from a tube and analyzed for dye fluorescence to evaluate the effects of the neutron access tubes on preferential water movement.

Thirty-two undisturbed soil cores were collected from the west walls of the trenches and at several depths beneath the corn rows and furrows for measurements of saturated hydraulic conductivity. Most of these samples were obtained by pushing a 5-cm i.d. by 8-cm-long thin-wall brass tube horizontally into the wall of the trench. A vertically oriented core was also obtained adjacent to three of the horizontally oriented cores to estimate the vertical hydraulic conductivity. Saturated hydraulic conductivities (horizontal and vertical) were measured in a triaxial system with the constant-flow method (Olsen and others, 1988; 1991). Effective stresses were varied between 0.35 and 2.81 kg/cm². Each sample also was analyzed for grain-size distribution and bulk density.

About 80 undisturbed cores were collected from the two trenches for measurements of moisture-retention characteristics. These samples were obtained by pushing a 5-cm i.d. by 8-cm-long thin-wall steel tube into the wall of the trench. The cores were placed in Tempe cells and moisture retention was determined at tensions of 25, 50, 75, 100, 125, 150, 175, and 400 cm of water, according to the method of Richards (1965).

RESULTS AND DISCUSSION

The unsaturated zone at both the upland and lowland sites mostly consists of well-sorted fine- to medium-grained sand. Although the upper 1 m of soil at both sites is similar and composed of about 95 percent sand and 5 percent silt and clay, the unsaturated zone at the upland site is generally better sorted than at the lowland site (fig. 3; table 1). The grain size is coarser between the 1.0- and 2.0-m depths at the lowland site than at the upland site (fig. 3; table 1). Gopher burrows in the upper 0.5 m at the upland site are filled with sand grains that have diameters about 0.03 mm larger than grains in the surrounding matrix. Discontinuous iron-rich layers are present in the unsaturated zone between the 1- and 2-m depths at the upland site. The layers are 2- to 20-cm thick, are cemented with iron oxides, and contain an average of about 5 to 10 percent silt and clay compared to less than about 5 percent in adjacent horizons (M.D. Tomer, University of Minnesota, Soil Science Department, oral commun., 1993).

The total organic carbon (TOC) content at every stratigraphic horizon in the upper 0.6 m at the lowland site was typically about twice as large as that at the upland site (table 1). The TOC ranged from 0.38 to 1.10 percent at the lowland site and from 0.20 to 0.62 percent at the upland site (J.A. Lamb, University of Minnesota, Soil Science Department, written commun., 1993).

Most bulk densities ranged from 1.54 to 1.60 g/cm³ throughout the 2-m profile and were generally similar at each site (table 1). No significant difference in bulk density was evident between areas of coarse-grained
Figure 3. Saturated hydraulic conductivity and median grain size as a function of depth for soil samples collected from the upland and lowland sites, Princeton, Minn.
Table 1. Summary of unsaturated-zone properties for the upland and lowland sites at the Princeton, Minn., Management Systems Evaluation Area [cm/d, centimeters per day; number of analyses in parentheses, where appropriate]

<table>
<thead>
<tr>
<th>Unsaturated zone property</th>
<th>Upland Site</th>
<th>Lowland Site</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness, meters</td>
<td>4.0</td>
<td>2.8</td>
</tr>
<tr>
<td>Iron-rich, cemented layers present</td>
<td>yes</td>
<td>no</td>
</tr>
<tr>
<td>Grain size in upper meter (median), millimeters</td>
<td>0.19 (27)</td>
<td>0.23 (57)</td>
</tr>
<tr>
<td>Grain size between 1 and 2 meters (median), millimeters</td>
<td>0.20 (13)</td>
<td>0.40 (41)</td>
</tr>
<tr>
<td>Total organic carbon content in upper 0.6 meters (median), percent</td>
<td>0.35 (8)</td>
<td>0.74 (8)</td>
</tr>
<tr>
<td>Bulk density in upper meter (median), October 22, 1991, grams per cubic centimeter</td>
<td>1.56 (89)</td>
<td>1.58 (57)</td>
</tr>
<tr>
<td>Volumetric moisture content in upper meter (median), October 22, 1991, dimensionless</td>
<td>0.09 (89)</td>
<td>0.12 (57)</td>
</tr>
<tr>
<td>Volumetric moisture content between 1 and 2 meters (median), October 22, 1991, dimensionless</td>
<td>0.08 (33)</td>
<td>0.06 (41)</td>
</tr>
<tr>
<td>Saturated hydraulic conductivity in upper meter (median), centimeters per second</td>
<td>4.3x10^-3 (5)</td>
<td>3.5x10^-3 (7)</td>
</tr>
<tr>
<td>Saturated hydraulic conductivity between 1 and 2 meters (median), centimeters per second</td>
<td>5.7x10^-3 (5)</td>
<td>7.2x10^-3 (5)</td>
</tr>
<tr>
<td>Approximate dye transport time through the unsaturated zone, July 5 through October 23, 1993, cm/d</td>
<td>5.3</td>
<td>3.7</td>
</tr>
<tr>
<td>Average depth of visible dye beneath corn rows, meters</td>
<td>0.1</td>
<td>0.04</td>
</tr>
<tr>
<td>Average depth of visible dye beneath furrows, meters</td>
<td>0.4</td>
<td>0.2</td>
</tr>
</tbody>
</table>

sand filling gopher burrows and the surrounding fine-grained matrix.

Volumetric moisture contents in the upper 1 m, and particularly in the upper 0.6 m, at the lowland site were slightly greater than at the upland site (table 1). Most moisture contents ranged from 0.07 to 0.11 at the upland site and from 0.05 to 0.11 at the lowland site. Below a depth of 1 m, moisture contents at the lowland site were slightly less than those at the upland site (table 1). The smaller moisture contents below a 1-m depth at the lowland site are likely due to the coarser grain size compared to that at the upland site.

Saturated hydraulic conductivities (K) at the upland and lowland sites generally reflect the measured differences in grain-size distribution and TOC content. The median horizontal K in the upper 1 m of the unsaturated zone is slightly greater at the upland site than at the lowland site (fig. 3; table 1), probably because the TOC content is greater at the lowland site than at the upland site. Because the grain size is coarser below 1 m at the lowland site, the median horizontal K is about twice as large as the horizontal K for the same depth interval at the upland site. The median vertical K of 5.4x10^-3 cm/s, based on the samples collected vertically, is similar to the median horizontal K (table 1).

Preliminary results of moisture-retention studies are available only for the upland site. The average moisture-retention curve plotted from data for 31 samples is shown in figure 4 and is typical of a medium-grained sand. The standard deviation decreases with decreasing tension and increasing moisture content between soil tensions of 0 and 25 cm. The standard deviation is greatest between soil tensions of 25 and 75 cm and is relatively constant between soil tensions of 175 and 400 cm.

The distribution of dye in the unsaturated zone was highly variable at both sites. The average depth of visible dye beneath the corn rows and furrows at the
The dye generally moved below land surface in vertically elongated pulses rather than as a uniform front to a single depth. Most of these pulses occurred below areas of topsoil that were about 1 to 3 cm lower than the surrounding topsoil. Because of runoff, dye collected in these microtopographic depressions, resulting in preferential movement of dye below land surface.

Dye visibly moved around heterogeneities in the unsaturated zone, such as the upland site gopher burrows that were filled with sand that was coarser than the surrounding soil matrix. The dye moved around gopher burrows that were less than about 8 cm in diameter. This phenomenon of unsaturated movement of water around coarser sand was first described by Haines (1930) and has been termed funnel flow (Kung, 1990). Water moves into the coarser sand when the suction of water within pores in the overlying finer sand is greater than it is in the coarse sand. This movement of water into the coarser sand is termed a Haines jump (Haines, 1930). Dye movement indicated that a Haines jump occurred through the middle of gopher burrows that were greater than about 10 cm in diameter.

The median dye concentration adjacent to neutron access tubes was about 2 times greater than the median concentration at a radial distance of 0.05 m. The greater dye concentrations adjacent to the neutron access tubes probably resulted from development of plant roots around the tubes along which dye moved preferentially. Warmer air temperatures within each tube, compared to the ambient soil temperature, likely caused the roots to grow around the tubes. These results could indicate that soil-moisture contents determined by use
of the neutron access tubes are greater than the average volumetric moisture content in the surrounding soil matrix. Additional research is needed to evaluate these apparent differences in moisture content.

About 100 days after application, the dye was detected at all five sampling ports in the multiport well between 0.5 and 2.0 m below the water table at the upland and lowland sites. Figure 2 illustrates the concentration of dye in ground water about 1.0 m below the water table at the lowland site from July 5 through November 5, 1991. Concentrations of dye ranged from 0.01 to 0.8 μg/L from late October through December 1991, and the dye was not detected after January 9, 1992. The greatest concentration of dye was detected on October 23, 1991, at the lowland site (0.5 μg/L) and on January 9, 1992, at the upland site (0.8 μg/L).

Assuming that the average ground-water velocity was about 10 cm/d and that some of the dye moved conservatively with the ground water, the travel time for the dye from the point where the dye reached the water table to the multiport well sampling ports (2.5 m) was about 25 days. Subtracting this 25-day travel time through the saturated zone, from the total travel time of about 100 days, yields an estimated 75-day conservative travel time for dye through the unsaturated zone. Therefore, the velocity of dye through the unsaturated zone was about 3.7 cm/d at the lowland site and 5.3 cm/d at the upland site on the basis of unsaturated-zone thicknesses of 2.8 and 4.0 m, respectively (table 1).

The dye moved 2 m vertically through the saturated zone over a horizontal distance of about 9 m, whereas less than 0.2 m of vertical movement was predicted with a steady-state ground-water-flow model of the saturated zone. Detection of the dye in all sampling ports at both sites indicates a much steeper vertical component of ground-water flow than that predicted by the conceptual ground-water-flow model used for the MSEA study.

SUMMARY AND CONCLUSIONS

The distribution of dye in the unsaturated zone was highly variable at both sites. The average depth of visible dye beneath the corn rows and furrows at the upland site was about twice as large as at the lowland site. The dye was likely adsorbed to the organic matter, which was greater at the lowland site than at the upland site. Dye movement was greatest beneath the furrows and least beneath the corn rows. The greater dye movement beneath the furrows was largely due to runoff of the dye solution from the side-slope areas of adjacent corn rows. The dye generally moved below land surface in vertically elongated pulses rather than as a uniform front at one depth. Most of these pulses occurred below areas of topsoil that were about 1 to 3 cm lower than the surrounding topsoil. Dye moved preferentially in the vicinity of corn plant roots; these areas, however, were narrower than the areas of dye movement beneath the furrows. Dye moved around heterogeneities in the unsaturated zone at the upland site, such as gopher burrows that were filled with sand that was coarser than the surrounding soil matrix. Dye moved around gopher burrows that were less than about 8 cm in diameter.

Dye movement indicated that a Haines jump occurred through the middle of gopher burrows that were greater than about 10 cm in diameter. The median dye concentration adjacent to neutron access tubes was about 2 times greater than the median concentration at a radial distance of 0.05 m. These results may indicate that soil-moisture data collected from neutron access tubes are greater than the average volumetric moisture content in the surrounding soil matrix. Visible dye distribution was not strongly correlated with soil bulk density, saturated hydraulic conductivity, moisture-retention characteristics, or volumetric moisture content.

About 100 days after application, the dye was detected at all five sampling ports between 0.5 and 2.0 m below the water table at the upland and lowland sites. The transport time for the dye from the point where the dye reached the water table to the multiport well sampling ports (2.5 m) was about 25 days. The transport velocity of dye through the unsaturated zone was about 3.7 cm/d at the lowland site and 5.3 cm/d at the upland site on the basis of unsaturated-zone thicknesses of 2.8 and 4.0 m, respectively. The dye moved 2 m vertically through the saturated zone over a horizontal distance of about 9 m, whereas less than 0.2 m of vertical movement was predicted with a steady-state ground-water-flow model of the saturated zone.

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Nitrogen Uptake and Soil Water Variability Across a Sand Plain Landscape

By J.A. Lamb¹, M.D. Tomer², J.L. Anderson³, and R.H. Dowdy⁴

Abstract

Research at the Northern Cornbelt Sand Plains Management Systems Evaluation Area at Princeton, Minnesota, was conducted to characterize the variability of whole-plant nitrogen uptake and soil-water content under a continuous corn-cropping system. The soil was a Zimmerman fine sand (mixed, frigid, Alfic Udipsamment). Nitrogen fertilizer was applied uniformly in 1991 and 1992. In 1991 and 1992, corn whole-plant samples were collected in 15-meter intervals along a 244-meter-long transect to determine nitrogen uptake. In 1992, plastic neutron-moisture-meter access tubes were placed to a depth of 2 meters every 20 meters along the same transect. Nitrogen uptake ranged from 115 to 157 kilograms nitrogen per hectare in 1991 and 92 to 132 kilograms nitrogen per hectare in 1992. Mean uptake of nitrogen was 24 kilograms per hectare greater in 1991 than it was in 1992. Soil-water content ranged from 10 to 15 centimeters for the upper 1.7-meter depth interval on July 23, 1992. The area where nitrogen uptake in 1992 was least is a sideslope area where the surface soil was driest. Leaching may have occurred during recharge events during the growing season at this and positions in the terrain.

INTRODUCTION

The Northern Cornbelt Sand Plains Management Systems Evaluation Area (MSEA) program is a multi-agency, multistate initiative to evaluate the effects of present and modifications to present agricultural management systems on water quality in a sand plain areas in Minnesota, North Dakota, South Dakota, and Wisconsin. The Northern Cornbelt Sand Plains MSEA program is a cooperative study primarily between the U.S. Department of Agriculture-Agricultural Research Service, the University of Minnesota Soil Science Department, and the U.S. Geological Survey.

Ground water contamination from agricultural management systems is caused by numerous complex processes. An objective of the MSEA project is to evaluate agricultural systems with the goal of minimizing adverse effects of agricultural management practices on ground water. Nitrogen (N) fertilizer is necessary for profitable corn production; however, N fertilizers combined with N mineralized from soil organic matter can be major sources of ground-water contamination. N fertilizer traditionally has been uniformly applied on production fields. The Northern Cornbelt Sand Plains MSEA has been investigating the effect of landscape variability on N uptake by crops and on soil-water content. N in soils and fertilizer can be removed by processes such as plant uptake and removal, leaching of nitrate-N through the soil, erosion of soil, and denitrification by bacteria. Because of typically high infiltration rates for the sandy soils at the Northern Cornbelt Sand Plains MSEA, offsite losses of N resulting from erosion are negligible. The purpose of this paper is to examine the relation of N uptake by corn to soil-water content across a typical sand-plain terrain.

MATERIALS AND METHODS

The Northern Cornbelt Sand Plains MSEA, Princeton, Minn., site (45°31'34"N. and 93°37'8"W.) was established in 1991 on the Anoka Sand Plain
located 90 kilometer (km) northwest of Minneapolis, Minn. The predominant soil is a Zimmerman fine sand (mixed, frigid, Alfic, Udipsamment). Topographic relief at the 64 hectare (ha) Princeton MSEA is less than 3 meters (m). Generally, the unsaturated zone consists of fine- to medium-grained sand, and the saturated zone consists of medium- to coarse-grained sand. Discontinuous layers of silt and very fine-grained sand as thick as 20 centimeters (cm) are present in the unsaturated and saturated zones. A predominantly clayey till underlies the surficial aquifer. During 1991, the average depth to the water table was about 3.7 m below land surface, and the saturated thickness ranged from 4 to 16 m. The direction of ground water flow generally is from west to east at about 8 centimeters per day (cm d$^{-1}$). Ground-water recharge rates generally range from 10 to 20 centimeters per year (cm yr$^{-1}$).

Five 1.8- to 2.7-ha cropped areas are aligned with the predominant direction of ground-water flow at the Princeton MSEA (fig. 1) where three agricultural management systems are being evaluated: (1) Corn-soybean crops are rotated under ridge (conservation) tillage, split N application, N application adjusted for N mineralized from previous legume crop (soybean), and


THESE ACCESS TUBES WERE USED TO MEASURE SOIL-WATER CONCENTRATION ON A VOLUMETRIC BASIS WITH A NEUTRON MOISTURE METER IN MULTIPLE-DAY SEQUENCES THAT BEGAN AFTER PREVIOUS SIGNIFICANT RAINFALL OR IRRIGATION. THE SOIL-WATER CONTENT FOR A SPECIFIC SOIL LAYER WAS DETERMINED BY MULTIPLYING THE SOIL WATER CONCENTRATION BY THE THICKNESS OF THE SOIL LAYER FROM WHICH THE DATA WERE DERIVED.

SAMPLES OF ABOVE-GROUND CORN-PLANT BIOMASS (GRAIN PLUS STOVER) WERE COLLECTED AT PHYSIOLOGICAL MATURITY FROM 2-M BY 1-M AREAS LOCATED EVERY 15 m ALONG THE TRANSECT. N CONCENTRATION WAS MEASURED BY MEANS OF KJELDAHL DIGESTION TECHNIQUES. WHOLE-PLANT N UPTAKE WAS THEN CALCULATED BY MULTIPLYING THE BIOMASS TIMES N CONCENTRATION.

RESULTS AND DISCUSSION


![Figure 2](https://example.com/image2.png)

**Figure 2.** Corn whole-plant nitrogen uptake in kilograms per hectare for continuous corn in 1991 and 1992 at the Princeton, Minnesota Management Systems Evaluation Area along transect A-A' (transect shown in fig. 1).

<table>
<thead>
<tr>
<th>Year</th>
<th>Nitrogen uptake (kilograms per hectare)</th>
<th>Coefficient of variation (percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>Range</td>
</tr>
<tr>
<td>1991</td>
<td>136</td>
<td>115 - 157</td>
</tr>
<tr>
<td>1992</td>
<td>112</td>
<td>92 - 132</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Year</th>
<th>Plant biomass (megagrams per hectare)</th>
<th>Coefficient of variation (percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>Range</td>
</tr>
<tr>
<td>1991</td>
<td>14.3</td>
<td>11.6 - 18.1</td>
</tr>
<tr>
<td>1992</td>
<td>14.5</td>
<td>10.7 - 18.2</td>
</tr>
</tbody>
</table>
Figure 3. Cross section of the (a) wettest and (b) driest soil-water conditions measured during the 1992 growing season along transect A-A' (transect shown in fig. 1).
160 to 165 m from the western end of the field in both years, whereas less than average N uptakes occurred in the area 110 to 150 m along the transect (fig. 2). The N uptakes are local maximums in 1991 and local minimums in 1992 at three locations along the transect (23, 69, and 177 m). The N uptakes are local maximums in 1992, local minimums in 1991 at two locations along the transect (54 and 192 m). These results suggest that the large differences in N uptake occur in similar places each year. There is not a strong correlation between years and location for N uptake (r = 0.24).

Soil in the vadose zone is not homogeneous. Thin illuvial horizons (lamellae) are present in the 1- to 1.7-m-depth interval throughout the Princeton, Minn. MSEA, usually in topographically high terrain. These layers may retard or divert soil-water movement, thereby affecting potential loss of N by leaching and plant N uptake. The spatial variability of soil-water content illustrated in figure 3 is caused by the perching of soil water above the lamellae. The greatest perching of soil water occurred at the hilltop position in the area 125 and 175 m along the transect (fig. 3). Rates of water loss caused by crop use or drainage after rainfall or irrigation were slower where the degree of perching was greatest. During dry periods in the growing season, soil-water content in the upper 1-m depth interval was least along sideslope positions, which coincide with areas of least N uptake, particularly the west-facing slope in the area 110 to 140 m along the transect. N uptake by plants may have been limited by poor surface- and subsurface-water retention relative to that at other locations, resulting in reduced crop growth and an increased potential for leaching of N.

After irrigation on July 23, 1992, soil-water content in the 1.7-m depth interval ranged from 10 to 15 cm. Soil-water content was least at the western end of the transect, where subsoils are coarse and lamellae are absent, and greatest in upland positions where soil-water perching occurs. Soil-water content also was small on sideslope positions where the surface soil horizon is thinner than it is along the rest of the transect. Water loss from crop use and drainage during July 23-August 3, 1992, ranged from 3.5 to 5.5 cm. If the differences in soil-water content and soil water losses from crop use and drainage were considered, there is a potential for variations in the amount of N that could be transported vertically to ground water, even over a relatively short horizontal distance of the transect (244 m).

Considering soil-water content and N uptake, the area where plant uptake of N was least was also the area where the potential for leaching of N was greatest (sideslopes). The variability in plant N uptake and soil-water content indicate that the processes involved in the removal of N from the soil and the transport of N to the ground water are complex. Accordingly, monitoring the effects of an agricultural-management practice on ground-water quality and in identifying the predominant process affecting the movement of N to the ground water will be difficult. These results strongly suggest that knowledge of the location of a particular site with a managed area is important in interpreting effects of agricultural-management systems.

### SUMMARY

Variability in corn N uptake and soil-water content was very complex along a 244-m-long transect at the Northern Cornbelt Sand Plains MSEA near Princeton, Minn. N uptake by corn had ranged from 115 to 157 kg ha⁻¹ in 1991, and 92 to 132 kg ha⁻¹ in 1992. The mean N uptake was 24 kg ha⁻¹ greater in 1991 than it was in 1992, indicating that annual fluctuations in N uptake occur and were similar in 1991 and 1992 as measured by range in uptake and coefficient of variation. The correlation of N uptake and location along the transect during 1991 and 1992 was not good (r = 0.24). Soil-water content in the upper 1.7 m depth interval along the transect varied from 10 to 15 cm on July 23, 1992. The least N uptake occurred in 1991 and 1992 in a sideslope area where surface soils were dry because of a lack of subsurface lamella to slow vertical water movement. Therefore, the loss of N by leaching may be increased in sideslope areas.

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Geophysical Investigations of Heterogeneity and Scale at the Princeton, Minnesota, Management Systems Evaluation Area

By Jeffrey E. Lucius and Gary R. Olhoeft

Abstract

The U.S. Geological Survey collected more than 1 gigabyte of ground penetrating radar (GPR) data in 1991 at the Princeton, Minnesota, Management Systems Evaluation Area (MSEA) to generate detailed images of the subsurface and to determine the three-dimensional spatial variability of hydrogeologic properties. The Princeton MSEA is located on the Anoka glacial outwash sand plain northwest of Minneapolis-St. Paul. The GPR system transmitted electromagnetic pulses that propagated through the ground. The pulses were partially reflected back to the GPR antennas when they encountered changes in electrical properties (which are controlled by water content, bulk density, lithology, and porosity). The GPR data were computer processed to produce geometrically correct images of the subsurface. Reflector continuity, amplitude, configuration, and spatial frequency were analyzed in the GPR images to determine lithologic structure, depositional processes, moisture content, stratification patterns, and grain-size distributions. Changes in water-table capillary fringe thickness, areas of possible focused recharge, areas consisting of eolian or other fine-grained deposition, and undulations of the till surface were identified. The GPR images were also correlated with lithology logs from sampling wells. For agricultural sites with very little or no clay near the surface, ground penetrating radar offers a fast, cost-effective, high-resolution method for extending information acquired at

INTRODUCTION

Agricultural pesticides, herbicides, and fertilizers are intended for the plant and root zone of the shallow subsurface. Sometimes, however, these chemicals migrate downward into the water-saturated zone and affect ground-water quality. The MSEA program is part of a multiscale, interagency project to evaluate the effects of agricultural practices on ground-water quality. An objective of the MSEA program is to improve our understanding of the processes and factors affecting the transport and fate of agricultural chemicals in a particular hydrologic system. The U.S. Geological Survey (USGS) has been conducting investigations to determine the three-dimensional spatial variability of hydrogeologic properties by use of GPR. The overall objective was to determine the usefulness of geophysical methods to hydrologic investigations in an agricultural setting. The specific objectives were to (1) generate high-resolution images of the subsurface geology and (2) characterize the hydrogeologic heterogeneity in terms of length-scales and statistical distributions—important factors in understanding three-dimensional patterns of ground-water flow.

The investigations were conducted at the MSEA (fig. 1) located on the Anoka Sand Plain near Princeton, Minnesota (approximately 100 kilometers (km) northwest of Minneapolis and St. Paul) during January, April, and October of 1991. The near-surface material at the site is glacial outwash that consists of mixtures of fine-to-medium and medium-to-coarse sand and gravel with discontinuous, thin silty layers (Delin and others, 1992). A loamy sand soil is present at the surface. The outwash is underlain by glacial till below the water table. Topography at the site is relatively flat; relief is about three meters (fig. 1). Average annual precipitation is about 76 centimeters (cm).

The GPR system used in this study was a Subsurface Interface Radar (SIR™) System-7 manufactured by Geophysical Survey Systems, Inc. The system
Figure 1. Land-surface topography at the Princeton, Minnesota, Management Systems Evaluation Area.
The GPR horizontal-sampling interval along the traverses was about 2 to 3 cm; this interval varied slightly according to antenna towing speed. The vertical sampling interval depends on how the GPR system was adjusted; and ranged from about 2 to 4 cm. Vertical resolution is a function of antenna frequency, signal wavelength in the ground, data-collection rate, and speed of the radar-wave propagating in the ground. Although the GPR system can detect thin layers, those layers must be separated by about one wavelength or constructive and destructive interference of closely-spaced reflected waveforms will complicate interpretation. The estimated radar wavelengths in the ground (using a relative dielectric permittivity of 4 measured in dry sand at the site) were 1.8 meter (m) for the 80-MHz antennas, 0.5 m for the 300-MHz antennas, and 0.3 m for the 500-MHz antennas.

The GPR data were computer processed to correct for geometric distortions inherent in the data-collection process and to produce a more tractable data set for characterization of the subsurface or estimation of the hydraulic properties. A background trace (the average of all traces in a traverse) was subtracted from each raw trace to minimize system noise in the data. A running-average filter, approximately 0.5 m in length, was applied to the raw data to improve the signal-to-noise ratio. For display, data placement was horizontally corrected for variations in towing speed. Then a time-to-depth conversion was determined (based on bulk relative dielectric permittivity of 4 above the water table and 6.5 below the water table and above the till) and used to convert the recorded time sections into approximate depth sections; static corrections were applied to adjust for elevation changes. The result was (approximately) geometrically correct images of the subsurface.

Gray-scale images of processed 300-MHz data along two west-to-east traverses are shown in figure 2 (locations of the two traverses are shown in fig. 1). Elevations are approximate because the time-to-depth conversion (using a relative dielectric permittivity of 4 for the entire section) is approximate. The vertical exaggeration of 15 causes the dips of many features and the topography to appear much steeper than they really are. Reflections that are either very light or very dark in the GPR images indicate subhorizontal features. The banding in the top 1 m of each image is caused by near-field interference of the 300-MHz radar wave and is not due to subsurface reflections.
Figure 2. Gray-scale images of computer-processed 300-MHz ground penetrating radar data along west-to-east traverses, rows 1 and 8, at the Princeton, Minnesota, Management Systems Evaluation Area. (Locations are shown in fig. 1.)
The strongest and most continuous reflector in these two images is from the water table, located at about 294.5 m above sea level. The water-table reflector is easy to identify in the image of row 1 between 70 to 400 m horizontal distance and in the image of row 8 between 50 and 470 m horizontal distance. This suggests the capillary fringe is thin and that sediments near the water table are coarse-grained. East of these areas in both images, the water-table reflector becomes harder to identify because the relatively thick capillary fringe in fine-grained sediment causes a gradual transition in dielectric properties and reduces the clarity of the reflection.

The remaining reflections in these two images are generated by small changes in water content above the water table and by changes in lithology and bulk density below the water table. Analysis of reflection facies (see, for example, Sangree and Widmier, 1979; Beres and Haeni, 1991) can be applied to these images. The area west of 400 m horizontal distance in row 1 is dominated by simple, layered reflections of moderate amplitude and low spatial frequency. This indicates thin to moderately thick, horizontally layered, coarse sand and gravel with only slight contrasts in electrical properties. East of 400 m, the reflections are more chaotic, having higher amplitude and spatial frequency, suggesting the presence of mixed layers of sand, silt, and gravel of variable thickness and extent.

For row 8, the water-table reflector between 160 and 320 m horizontal distance, at an elevation of about 294 m, appears to bulge upward near the low area at 240 m horizontal distance, indicating this low area might be a source of enhanced or focused recharge. Delin and Landon (1993) have discovered this to be true for one lowland area on the site and indicate that focused recharge could be occurring at other lowland areas. These areas might contribute to focused transport of agricultural chemicals to the ground water. At 600 m horizontal distance, there appears to be a "depression" in the layering 2 m below the surface. The solid gray area above the reflector indicates homogeneous deposition, perhaps the result of eolian deposition of fine-grained material in low-lying areas. Eolian silt and sand are found at the surface over several areas on the site.

Gray-scale images of processed 80-MHz data along a west-to-east traverse are shown in figure 3. The location of the traverse is shown in figure 1. The vertical exaggeration is 10 in the upper image. The lower image shows part of the traverse between 140 and 280 m horizontal distance without vertical exaggeration. The banding caused by near-field interference of the 80-MHz radar wave covers about 3 m at the top of each radar image, effectively concealing the water-table reflector at 294.5-m elevation. The lowest strong reflector in each image is from the glacial till underlying the outwash sands and gravels. Undulations of the till surface are apparent. Comparing the upper and lower images also shows how vertical exaggeration distorts the GPR reflectors. The reflectors in the lower image indicate the structural complexity in the depositional sequence on this part of the Anoka glacial outwash plain.

CORRELATION OF REFLECTORS AND LITHOLOGY LOGS

Several of the GPR traverses were near USGS sampling wells. The driller's lithology logs were examined to determine how well they correlated with the GPR images. An example for well MC-11 near the start of GPR traverse row 16 is shown in figure 4 (see fig. 1 for locations). A possible correlation of the log to the GPR reflectors is indicated by the lines connecting the log to the GPR image. "WT" is the water-table reflector. Ground surface at MC-11 is slightly higher than it is at the western end of Row 16. In general, the logs do not correlate well with the GPR image, in part, because the sediments are mixed by the power auger used to drill the wells and can only be approximately located. Beres and Haeni (1991) note that correlation commonly improves when the core is a continuous sample. There can be several other causes for the poor correlation. Variations in porosity, which change the water content and, therefore, the electrical properties, may be not be uniquely related to variations in lithology. In addition, constructive and destructive interference of the reflected GPR waves may hide closely spaced layers, create "false" layers, and/or combine several layers to appear as only one.

DISCUSSION

There are several scales of investigation in the MSEA program: core sample, small, field, and regional scales. The resolution and sampling of the GPR system are probably too coarse to be useful at the scale of a core sample (millimeters to several centimeters), and the size of the field site is too small for regional-scale investigations (several kilometers). However, GPR data can be useful at small-scale (less than 1 m) and field-scale (tens to hundreds of meters) investigations,
Figure 3. Gray-scale images of computer-processed 80-MHz ground penetrating radar data along west-to-east traverses, row 5B, at the Princeton, Minnesota, Management Systems Evaluation Area. (Location is shown in fig. 1.)
Figure 4. Summary of lithologic log for USGS well MC-11 near the start of ground penetrating radar traverse row 16 at the Princeton, Minnesota, Management Systems Evaluation Area. (Locations are shown in fig. 1.)

depending on antenna frequency and spacing of traverses.

At all scales, hydraulic-flow patterns are observed to be three dimensional and controlled by hydrogeologic heterogeneity. Uncertainties caused by the spatial variability of hydraulic properties, such as unsaturated hydraulic conductivity, affect the ability to model and forecast flow and transport of solutes in porous media. GPR can provide the additional information required to extend hydrologic information obtained at test holes and wells to much larger areas. In some cases, GPR data can directly provide hydrologic information such as moisture content (Duke, 1990; Sutinen and others, 1992) or transmissivity (by repeated measurements across time to track the position of moving fluids or wetting fronts; Sander and others, 1992).

GPR measurements record signals that are interpreted as reflections from boundaries of hydrogeologic units with contrasting electrical properties (relative dielectric permittivity and electrical conductivity)
controlled by water content, bulk density, lithology, and grain-size distribution. Because the signals are reflected by contrasts between layers, the processed images give good structural and geometric information, whereas information about absolute properties must be deduced by modeling individual signals (Duke, 1990; Powers and others, 1992). The relation between GPR measurements and hydraulic properties is complex. However, an empirical relation between relative dielectric permittivity and volumetric water content for glacial materials can be determined (Sutinen and others, 1992). An infiltration test has been planned so that the GPR system can be used repetitively over an area to determine the progressive movement of the wetting front and thereby infer vertical hydraulic conductivity (see Olhoeft, 1985; Sander and others, 1992).

The GPR system may prove extremely helpful to hydrologists in characterizing a new site. However, in an agricultural setting, the GPR system cannot directly detect very low concentrations of pesticides or fertilizers in the subsurface. If the site is relatively free of clay minerals, GPR data can be useful in (1) determining depth and topography of bedrock or other formation (such as till); (2) measuring variations in the water table (Shih and others, 1986); (3) detecting the effects of well draw-down tests; (4) identifying perched water tables; (5) determining the lateral variations of lithologies (extent and thickness) near test wells and between wells; (6) measuring the type and thickness of soil horizons with the high-frequency antennas (Collins, 1992; Doolittle and Asmussen, 1992); and (7) detecting the presence of preferential flow paths (Donohue and others, 1992).

GPR-data collection and processing is relatively fast and cost effective in comparison to other methods that might collect near-continuous data, such as close-spaced drilling or trenching. The GPR system also has the advantage of being noninvasive. For each of the 780-m-long GPR traverses, approximately 15 minutes were needed to collect the GPR data using a pickup truck and three people. The 80 to 110 topographic stations along a traverse took about 1 hour to survey using an electronic total station connected to a pocket computer. Processing GPR data in a computer is not necessary in all applications, as some problems do not require any enhancement or geometric correction of the data. A 780-m traverse of GPR data required 1 to 2 hours to process (using software developed by the authors) and produce an image (stored on disk as an Encapsulated PostScript (EPS) file) such as those shown in the figures.

CONCLUSIONS

Understanding the hydrogeology of a site is integral to determining the potential for ground water contamination by surface-applied agricultural chemicals. Analysis of the geometrically corrected GPR images shows that reflector continuity, amplitude, configuration, and spatial frequency reveal details of the subsurface unavailable by point-source measurements provided by drilling. Lithologic structure, depositional processes, moisture content, stratification patterns, and grain-size distributions can all be interpreted from GPR data using antennas of appropriate frequency and images displayed at appropriate scale. Ground penetrating radar offers a fast, cost-effective, high-resolution method for extending information acquired at test wells and for presenting a comprehensive view of subsurface structure. With the addition of computer processing, GPR data can also produce information about hydrologic properties. GPR does not work at all sites, but for areas with very little or no clay near the surface, it should be considered as a preliminary study tool and as a geophysical technique to provide better understanding of geologic and hydrologic information.

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Abstract

A broad interagency research program is being conducted near Princeton, Minnesota, to investigate possible advantages of various modifications to existing farming techniques with the goal of decreasing contamination of ground-water and surface-water supplies by agricultural chemicals. Most of the program is focused on a 160-acre test farm, with the intention that the results from the test farm be applied to other farms in the area. To facilitate extending the results to a broader region, a study was conducted to investigate regional effects of agricultural activity on nitrogen in ground waters and surface waters of the Battle Brook watershed. Shallow ground water has received the greatest inputs of nitrate-nitrogen. Concentrations of nitrate-nitrogen (nitrate-N) exceeding 10 milligrams per liter (mg/L) as N are common near the water table. Nitrate-N concentrations decreased rapidly with depth (deeper than about 8 to 10 meters) in the saturated zone throughout the watershed, possibly because of mixing with uncontaminated waters or because of denitrification. Extensive wetlands in the area are fed by the discharge of shallow ground water, yet nitrate-N was not detected in any wetland waters. Biological activity in the wetland and its sediments is capable of decreasing nitrate-N concentrations. Monthly to bimonthly sampling of a piezometer near the water table at the Princeton test farm during July, 1991 to August, 1992, shows that nitrate-N concentrations varied between 13 and 25 mg/L in response to seasonal recharge events. The magnitude of the variation decreased with depth; about 2 meters below the water table, nitrate-N concentrations ranged from 12 to 17 mg/L.

INTRODUCTION

The Management Systems Evaluation Area (MSEA) program is a multiscale interagency program with participation by the U.S. Geological Survey, the U.S. Department of Agriculture, the Cooperative State Research Service, and the U.S. Environmental Protection Agency. The northern Midwest of the United States was selected for this program because this area receives approximately 60 percent of fertilizers and pesticides used in the United States annually (Burkhart and others, 1990). Extensive nitrate-N contamination has resulted from the continuous broad application of fertilizers in this region (see Power and Schepers, 1989). One of the five MSEA sites in this region is located near Princeton, Minnesota (fig. 1). The goal of the Princeton MSEA program is to evaluate the effects of best-management practices on ground-water quality through a variety of research projects being conducted at scales ranging from laboratory to small watersheds (about 90 square kilometers). The modified farming system being evaluated involves irrigated ridge-tillage in a corn and soybean rotation, whereas the prevailing farming system in the surrounding Anoka Sand Plain involves irrigated conventional tillage in continuous corn.

The Princeton MSEA program is primarily designed for intensive study at the field scale. The
EXPLANATION OF SAMPLING SITES
- Water samples from wells less than ten m deep
- Water samples from wells greater than ten m deep
- Surface-water samples
- Outlets of drain tiles
- Multilevel piezometers

Figure 1. Location of the Battle Brook watershed near Princeton, Minnesota.

The purpose of this study was to investigate the ground and surface-water chemistry in the Battle Brook watershed in order to link the results of the effects of farming systems at the field scale to the watershed scale. This report presents preliminary interpretations based on data collected during June, 1991-August, 1992, at the Princeton MSEA and in the surrounding watershed.

Battle Brook drains a low-relief, moderately wooded area of about 90 km² (fig. 1). The maximum elevation in the watershed is about 390 m above mean sea level and the mean elevation of Elk Lake, at the downstream end of the field area, is 346 m. Because the Battle Brook watershed is bounded by low-relief land-surface features, the surface-water divide shown in figure 1 is not likely to correspond to a ground-water divide. Regional ground-water flow in the southern half of the Battle Brook watershed is from approximately north to south in the surficial aquifer.
Surface-water samples

Ground-water samples from domestic wells:
- wells shallower than ten meters
- wells deeper than ten meters

Multilevel piezometer
- Drain tile

NITRATE AS NITROGEN, IN MILLIGRAMS PER LITER

Figure 2. Nitrate-nitrogen concentrations in ground-water and surface-water collected in the Battle Brook watershed near Princeton, Minnesota, June-July 1991.
the laboratory on samples collected and preserved in the field. Samples analyzed for cations were filtered through 0.45 μm silver-metal membrane filters and acidified to a pH less than 1 with concentrated hydrochloric acid. Cations were analyzed by inductively coupled plasma atomic emission spectroscopy (Lichte and others, 1987). Samples analyzed for anions were filtered through the same silver-metal membrane filters and chilled. The silver-metal filters kill any microorganisms in the sample. Anions were analyzed by ion chromatography with a mixed bicarbonate/carbonate eluent (Fishman and Pyen, 1979). Eluent and column conditions were optimized for maximum peak separation so individual concentrations of fluoride, chloride, nitrite, nitrate, phosphate, and sulfate could be resolved.

RESULTS AND DISCUSSION

All surface-water samples, except one, contained less than 1 mg/L NO$_3^-$-N (as N; fig. 2); most surface-water samples contained less than 0.02 mg/L NO$_3^-$-N. One sample from an irrigation ditch had a NO$_3^-$-N concentration of 1.2 mg/L NO$_3^-$ and most likely represents water pumped from an irrigation well shortly before the sample was collected. The temperature of this sample (15 °C) was significantly lower than any other surface-water sample (20 to 31 °C), which is consistent with a ground-water source.

Water samples from the shallow wells had nitrate-N concentrations ranging up to 25 mg/L. Water samples from deeper wells (greater than 10 m) generally had nitrate-N concentrations less than 0.3 mg/L. Thus, only shallow ground water is appreciably affected by agricultural practices. The degree to which the shallow ground water is contaminated varies considerably in the watershed; the greatest nitrate-N concentrations were detected in wells completed within or adjacent to farms (for example, multilevel piezometers in fig. 1), or in densely populated areas such as near Elk Lake (fig. 1). The lowest nitrate-N concentrations were in water from wells adjacent to wooded areas or in low-density residential areas away from farmed areas. Dissolved-oxygen concentrations were low (less than 1 mg/L) throughout the field area (Wanty and others, 1993). Lukashev and Onoshko (1989) found qualitatively similar results for nitrate-N sources and sinks in a region that includes industrial and agricultural activity as well as undeveloped land.

Wetlands occupy a large percentage of the surface area of the Battle Brook watershed (fig. 1). Water in Battle Brook is supplied by short-term surface runoff, or by discharge of shallow ground water. Numerous springs are found along the edge of the wetland area. Although the shallowest ground water generally had the greatest nitrate-N concentrations in areas outside the wetlands, none of the surface-water samples collected from the Battle Brook wetlands had detectable concentrations of nitrate-N. Nitrate-N may be taken up by plants in the wetland and by bacteria within the wetland sediments. Concentrations of nitrate-N in water from springs discharging at the edge of the wetland contained 1 to 2 mg/L nitrate-N, and 0.2 to 0.4 mg/L ammonium-N. Wetland pore waters, collected from water that filled shallow holes dug in the wetland, did not contain nitrate-N but did contain greater than 5 mg/L of ammonium-N. A series of experiments was conducted using two columns collected in the wetland; each column had a 15-cm diameter and was approximately 1 meter high. The columns contained about one-third each of wetland sediment, water and head space. The water column in both was spiked with nitrate and sulfate. Over the course of about two weeks, nitrate concentrations approached zero, while sulfate concentrations remained nearly unchanged. This result demonstrates the capability of the wetlands to take up nitrate-N. Therefore, wetlands may play an important role in attenuating anthropogenic nitrate-N concentrations. Continuing research is being conducted to determine the rate and extent of nitrate removal by wetlands as well as the seasonal variability of nitrogen concentrations in waters in and adjacent to the wetlands.

Samples were collected from three multilevel piezometers at the MSEA during July, 1991 - August, 1992 to evaluate temporal changes in the ground-water nitrate-N concentrations. Concentrations of nitrate-N in one of the multilevel piezometers are shown in figure 3. Nitrate-N concentrations in the upper 1 m of the saturated zone (ports 2, 3, and 4) varied greatly over the year, in contrast to the deepest port (port 6). Increases in nitrate-N concentrations in the upper meter of the saturated zone occurred during the growing season in 1991 and 1992. As shown for port 4, nitrate-N concentrations in ground water are lowest during the winter months. The variations in nitrate-N in the upper 1 m of the saturated zone occur because recharging water has greater concentrations of

Nitrate-N than does older ground water (Delin and Landon; 1993; 1996). Nitrate-N concentrations 2 m below the water table varied less because inputs of nitrate-N from recharge did not reach that depth. Similar variations in nitrate-N concentrations over time and with depth were observed in the other two multilevel piezometers sampled. Thus, the nitrate-N concentrations in wells screened at depths greater than about 2 m below the water table throughout the Battle Brook watershed are not likely to vary appreciably throughout the year. Persistently low nitrate-N concentrations in wells deeper than 2 m may indicate either that contaminated water does not infiltrate to those depths or that progressive denitrification occurs along ground-water flow paths. Either possibility would imply that the chemistry of the deeper ground water is less variable over time as compared to the shallow ground water, further suggesting that our single sampling period is representative of the longer time scale.

Nitrogen isotopes were measured in a selected suite of samples (11 ground-water samples and two fertilizer samples). These results are expressed in the conventional notation as the permil (‰) deviation from the atmospheric standard. Permil values are calculated using the formula:

$$\delta^{15}N = \left( \frac{^{15}N_{\text{sample}}}{^{15}N_{\text{standard}}} - 1 \right) \times 1000,$$

where $$R = \frac{^{15}N}{^{14}N}$$ in the sample or in the standard.

Nitrogen-isotope data for the ground-water samples from multilevel piezometers show $$d^{15}N$$ values from -1.5 to +2.8 ‰ relative to atmospheric nitrogen. These $$d^{15}N$$ values are quite close to those for fertilizers used in the field area, which ranged from -0.3 to +1.5 ‰ relative to atmospheric nitrogen, and are consistent...
with the interpretation that fertilizer is the main source of nitrate-N in the ground water at the MSEA. Such a source is consistent with the transient inputs of nitrate-N derived from excess fertilizer by recharging ground water throughout the growing season.

CONCLUSIONS

Infiltration of precipitation or irrigation in the Princeton, Minnesota study area leaches nitrate-N from the soil and carries it to the shallow ground-water regime. The greatest concentrations of nitrate-N in water from shallow wells were detected during the growing season (April through August of 1991 and 1992) following application of fertilizers. The greatest and most variable nitrate-N concentrations were observed in the shallowest wells. Nitrate-N concentrations in water sampled from drain tiles and multi-level piezometers (fig. 2), for example, commonly exceed 20 mg/L. Deeper within the saturated zone, nitrate-N concentrations are typically less than 0.3 mg/L.

Surface-water samples from the Battle Brook watershed generally contained less than 1 mg/L of nitrate-N. If the surface water is derived largely from discharge of shallow ground water, then most of the nitrate-N must have been removed from the shallow ground water by the time it discharges to the surface. Nitrate-N could be consumed by biota in the wetland, leading to the negligible nitrate-N concentrations observed in water in Battle Brook and the adjacent wetlands. Comparatively low concentrations of nitrate-N in ground-water samples from depths greater than 2 m below the water table likely result from microbial reduction of nitrate-N or from mixing with ground water that has relatively low concentrations of nitrate-N. Drain tiles, which remove water from low-lying fields and discharge it directly into the wetland, may be carrying significant amounts of dissolved nitrate-N into the surface-water regime, but that nitrate-N is rapidly and completely attenuated in the wetland environment.

REFERENCES


Chemical Loads of Nitrate, Atrazine, and Metolachlor in Walnut Creek Watershed near Ames, Iowa, 1991-92

By P.J. Soenksen¹, J.L. Hatfield², and D.J. Schmitz²

Abstract

Streamflow, stormflow, and tileflow were measured and sampled at numerous sites in the Walnut Creek watershed near Ames, Iowa, to determine the chemical discharges, loads, and yields of nitrate as nitrogen (nitrate-N) and the herbicides atrazine and metolachlor. From April 1991 to September 1992, nitrate-N yield was 58.4 kg/ha (kilograms per hectare), and atrazine and metolachlor yields were 4.5 g/ha (grams per hectare) and 7.3 g/ha, respectively, in streamflow from a 2,540-ha (hectare) subwatershed. Large chemical discharges and increases in cumulative loads were closely related to stormflow. Chemical loads were larger during the 1991 growing season, when soils were wet and stormflow occurred shortly after application of chemicals, compared to loads during the 1992 growing season when stormflow did not occur until several months after application of chemicals. Nitrate-N was transported during periods of base flow throughout the year; there were many periods when the herbicides were not detected.

For July-August 1992, a comparison of loads and yields in streamflow from the subwatershed was made to those in stormflow and tileflow from a 360-ha small basin within the subwatershed. The comparison indicates that most of the chemical load in streamflow was transported by tileflow, and little was transported by stormflow, even during stormflow. There were four periods of stormflow during July-August 1992, but there were none in the preceding 2 months. Nitrate-N yields were 8.0 kg/ha in streamflow, 0.06 kg/ha in stormflow, and 7.9 kg/ha in tileflow. Atrazine yields were 0.42 g/ha in streamflow, 0.010 g/ha in stormflow, and 0.50 g/ha in tileflow. Metolachlor yields were 0.42 g/ha in streamflow, 0.007 g/ha in stormflow, and 0.35 g/ha in tileflow. Comparison of daily yields, one during stormflow and one during base flow, with those from a field tile also indicate tileflow as the primary transporter of agricultural chemicals for this period.

INTRODUCTION

The presence of agricultural chemicals in the surface- and ground-water resources in many parts of the midwestern United States is a growing concern for the public and many government officials. As part of the Federal Water Quality Initiative (Onstad, Burkart, and Bubenzer, 1991), the Management Systems Evaluation Area (MSEA) program was established to evaluate the effects of current farming practices on water quality and to develop new practices that are both environmentally and economically sound. Five MSEA projects were selected to represent some of the principal hydrogeologic settings of the region. The Walnut Creek watershed near Ames, Iowa, is one of four primary research sites of the Iowa MSEA project. The U.S Geological Survey (USGS), through their Toxic Substances Hydrology Program, is cooperating with the Agricultural Research Service (ARS) and the Cooperative State Research Service of the U.S. Department of Agriculture in this research. Walnut Creek is also the site of the Environmental Protection Agency’s Midwest Agricultural Surface/Subsurface Transport and Effects Research (MASTER) project to evaluate the ecological and toxicological effects of agricultural chemicals.

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Because a number of extensively used agricultural chemicals are soluble in water, their environmental fate needs to be related to the major water-transport processes (Wauchope, 1978; Freeze and Cherry, 1979, p. 413). Gaining knowledge of the transport processes that affect chemicals and the conditions that control transport is an important step toward understanding the effects of existing management practices. This knowledge will aid in the selection of existing and the design of new management practices to minimize chemical transport from the point of application.

This paper documents the nitrate as nitrogen (nitrate-N), atrazine, and metolachlor transported by streamflow from a subwatershed of Walnut Creek from April 1991 to September 1992. A comparative analysis of the amounts transported during July-August 1992 to the amounts transported by stormflow and tileflow from two smaller basins within the subwatershed also is made. Chemical discharges, loads, and yields (load per unit area) are presented along with flow hydrographs and rainfall amounts.

WALNUT CREEK WATERSHED

Walnut Creek watershed is located in and representative of much of Midwest Land Resource Region 103 (U.S. Department of Agriculture-Soil Conservation Service, 1981), which covers much of north-central Iowa and southern Minnesota. The topography is nearly level with numerous potholes in the upper one-third of the watershed, nearly level or gently rolling in most of the other uplands, and steeper near the streams in the lower part of the watershed. Surficial deposits of till overlie carbonate bedrock. Till thickness is 60 to 90 m on the uplands, and total relief is about 60 m. Soils are in the Clarion-Niccollet-Webster association. The Clarion soils are well drained and moderately permeable on the uplands, whereas the adjacent Niccollet soils are poorly drained with moderate permeability. Natural drainage is poor in the upper part of the watershed, requiring the use of subsurface drainage tiles--many with surface inlets from potholes--and drainage ditches. Surface drainage areas are difficult to determine because of the nearly-level topography and subtle drainage features. In some cases, tile lines transport subsurface flow to an adjacent surface drainage basin. Large parts of some drainage areas, especially in the upper part of the watershed, may not contribute to stormflow but may contribute to tileflow via surface inlets and subsequently to streamflow.

Above where Walnut Creek flows across the South Skunk River alluvial plain, the watershed has a drainage area of about 5,100 ha that was divided into subwatersheds of about 1,300 to 2,500 ha (fig 1). The northwestern and southwestern subwatersheds are almost completely in row-crop agriculture and have large percentages of tile-drained land. The eastern subwatershed is steeper, with woodlands near some of the streams and a smaller percentage of tile-drained land. Study interests also included small basins of about 250 to 500 ha and field basins of about 5 to 25 ha. The locations of all USGS streamflow and stormflow sites and two ARS tileflow sites are shown in figure 1; sites also are listed in table 1 along with the study scale, surface drainage area, and types of flow evaluated. Of interest for this paper are sites 310, 220 and 110. The tileflow from site 220 contains stormflow from surface inlets to the tile, whereas site 110 has no surface inlet from the pothole field it drains. Rainfall data was collected at site 710. Study sites became fully operational as follows: site 310, streamflow, April 1991; site 220, stormflow, August 1991; site 220, tileflow, July 1991; site 110, tileflow, December 1991; site 710, rainfall, May 1991.

STUDY APPROACH

Discharge at streamflow and stormflow study sites was computed from recorded water-stage measurements and theoretical or measured stage-discharge relations (Rantz and others, 1982). Automatic stage measurements were made by float or balanced-beam manometer. Discharge at tileflow study sites was computed in real time by “flow meters” using recorded stage and a theoretical weir rating, or recorded stage and velocity measurements. Stage was measured with a pressure transducer, and velocity was measured with an electromagnetic sensor. Rainfall data were collected with a tipping-bucket rain gage. Data were recorded on electronic data collectors.

Water-quality samples were collected manually, on a weekly basis, and by automatic samplers. At streamflow and stormflow sites the samplers were triggered by the data loggers using real-time stage data and programmed decision aids. Tileflow samplers were triggered by timers in the samplers. Samples were analyzed for concentrations of nitrate-N, atrazine, metolachlor, alachlor, and metribuzin at the
ARS's National Soil Tilth Laboratory in Ames, Iowa, using the methods described by Pfeiffer and Steinheimer (1992). Nitrate-N concentrations were determined using a colorimetric method. The quantification limit was 1 mg/L. Pesticide analytes were extracted by use of a C₁₈ solid-phase extraction technique and analyzed with a gas chromatograph/mass spectrometer in a selective ion monitoring mode. For these analytes the detection limit in water was 0.2 μg/L.

Chemical discharges were computed from instantaneous values of concentration and the corresponding values of discharge. Discharge was computed for 5- and 15-minute intervals, depending on the site. Instantaneous concentration values were determined from time-concentration curves developed from the discrete sample concentrations. Generally, this involved linear interpolation between sample points, except just prior to stormflow periods where concentrations were kept at base-flow levels. Herbicide samples with concentrations below the detection limit were assigned a value of 0.1 μg/L, one-half the detection limit. Outliers were eliminated on the basis of data trends and comparison with the flow record. Chemical loads were computed by multiplying the chemical discharge by the appropriate time interval and appropriate unit conversion, and then summing the unit values of load as necessary.

Streamflow and stormflow sites were installed by USGS and ARS personnel, and tileflow and rainfall...
Table 1. Study sites in Walnut Creek watershed, Iowa

<table>
<thead>
<tr>
<th>Site number (fig. 1)</th>
<th>Site name</th>
<th>Study scale</th>
<th>Surface drainage area (hectares)</th>
<th>Type of flow evaluated</th>
</tr>
</thead>
<tbody>
<tr>
<td>110</td>
<td>Pothole field</td>
<td>Field basin</td>
<td>8.9</td>
<td>Tileflow</td>
</tr>
<tr>
<td>140</td>
<td>Walnut Creek tributary near Kelley</td>
<td>Field basin</td>
<td>13</td>
<td>Streamflow</td>
</tr>
<tr>
<td>220</td>
<td>South Branch Ditch of Walnut Creek at Kelley</td>
<td>Small basin</td>
<td>360</td>
<td>Stormflow</td>
</tr>
<tr>
<td>310</td>
<td>Walnut Creek at Kelley</td>
<td>Subwatershed</td>
<td>2,540</td>
<td>Streamflow</td>
</tr>
<tr>
<td>320</td>
<td>Walnut Creek near Kelley</td>
<td>Subwatershed</td>
<td>3,760</td>
<td>Streamflow</td>
</tr>
<tr>
<td>330</td>
<td>Walnut Creek near Cambridge</td>
<td>Watershed</td>
<td>5,100</td>
<td>Streamflow</td>
</tr>
</tbody>
</table>

1 Includes stormflow from surface inlets.

Sites were installed by ARS personnel. Routine site operation and data collection were done by the ARS, with quality control provided by the USGS at streamflow and stormflow sites. Streamflow, stormflow, and chemical discharge and load data were computed by the USGS. Tileflow and rainfall data were computed by the ARS.

RESULTS

The automatic sampling systems were effective in collecting a sufficient number of samples for analyses and subsequent development of time-concentration curves. More than 430 samples were collected at site 310 from April 1991 to September 1992, and many of those were collected during stormflow when concentrations were usually changing rapidly. Concentrations of nitrate-N in streamflow generally ranged from 10 to 20 mg/L during base flow, but concentrations decreased substantially, by as much as about 75 percent, during stormflow. Concentrations of atrazine and metolachlor generally were less than about 3.0 µg/L or less than the detection limit of 0.2 µg/L during base flow, but were as large 29 and 80 µg/L during stormflow in May 1991. The largest concentrations generally occurred on the rising limbs of the flow hydrographs or near the peaks. On the receding limbs of the hydrographs, concentrations decreased rapidly at first and then more slowly to very small levels.

Subwatershed Streamflow - Site 310

Sample analyses from April 1991 to September 1992 were used to determine daily loads of nitrate-N, atrazine, and metolachlor in a 2,540-ha subwatershed of Walnut Creek (fig. 2). A cumulative-load curve also is shown for each chemical along with the streamflow hydrograph. The cumulative loads and yields (not shown) for the entire period were 150,000 kg and 58 kg/ha for nitrate-N, 11,000 g and 4.5 g/ha for atrazine, and 19,000 g and 7.3 g/ha for metolachlor. For July-August 1992, the cumulative loads and yields were 20,000 kg and 8.0 kg/ha for nitrate-N, and 1,100 g and 0.42 g/ha for both herbicides. All chemical loads increased during stormflow; the herbicides almost exclusively so, but cumulative nitrate-N loads also increased during periods of base flow, even during the winter months. Most of the atrazine and metolachlor loads were transported during four different periods of stormflow from May 15 to June 4 of 1991 shortly after these chemicals were applied. Soils were very wet prior to this period. In 1992, by contrast, stormflow was less and it occurred later in the growing season resulting in decreased transport of herbicides.

Small-Basin Stormflow and Tileflow - Site 220

Data for July-August 1992 were examined for a 360-ha small basin (site 220) to help determine the sources of chemical loads at site 310. Hourly values of chemical discharge and stormflow, and chemical discharge and tileflow are shown in figures 3 and 4. Daily precipitation also is shown. Cumulative nitrate-N loads and yields (not shown) were 22 kg
Figure 2. Daily and cumulative loads of nitrate as nitrogen (nitrate-N), atrazine, and metolachlor, and daily streamflow at study site 310 (Walnut Creek at Kelly, Iowa).
Figure 3. Hourly and cumulative discharges and loads of nitrate as nitrogen (nitrate-N), atrazine, and metolachlor and hourly stormflow at study site 220 (South Branch Ditch of Walnut Creek at Kelley, Iowa), and total daily rainfall at study site 710.
Figure 4. Hourly and cumulative discharges and loads of nitrate as nitrogen (nitrate-N), atrazine, and metolachlor and hourly tileflow at study site 220 (South Branch Ditch of Walnut Creek at Kelley, Iowa), and total daily rainfall at study site 710.
and 0.06 kg/ha in stormflow (fig. 3), and 2,800 kg and 7.9 kg/ha in tileflow (fig. 4). Cumulative loads and yields of atrazine were 3.5 g and 0.010 g/ha in stormflow, and 180 g and 0.50 g/ha in tileflow. Cumulative loads and yields of metolachlor were 2.6 g and 0.007 g/ha in stormflow, and 130 g and 0.35 g/ha in tileflow. For each chemical the yield from tileflow at site 220 was similar to that from streamflow at site 310. The extremely small chemical yield in stormflow by comparison is expected because stormflow was so much less than tileflow. However, the chemical discharge rate in the stormflow was also much less than that in the tileflow. Together, these results would seem to indicate that, for the prevailing conditions, stormflow was not a major transport mechanism for any of these chemicals and that most of the chemical loads were transported by subsurface flow to the tile lines after leaching into the soil. This is reasonable because there were more than 75 mm of rainfall in July before any stormflow occurred, as shown in figures 3 and 4. If the stormflow at site 220 is representative of the flow into the surface inlets, then the effect of the inlets on the tileflow at site 220 was probably small. It is not known how significant stormflow was in transporting the much larger loads of atrazine and metolachlor in 1991 when stormflow occurred closer to the time following chemical application in the subwatershed.

Field-Basin Tileflow - Site 110

To investigate further the possible effects of surface inlets on the tileflow at site 220, some comparisons were made with the tileflow for a 8.9-ha field basin (site 110), which has no surface inlets. Yields of nitrate-N and atrazine are shown for each of the sites for two days during July-August 1992 (table 2). Data for July 16 is for a period of stormflow, the first in 2 months, and data for August 5 is for a period of base flow. Except for stormflow site 220, yields for all sites for both chemicals are very similar. On the basis of this comparison, it would seem that during July-August 1992 subsurface flow was the primary transport mechanism for each of the chemicals studied at site 220, even during periods of stormflow.

Summary

Streamflow, stormflow, and tileflow were measured and sampled at several sites in the Walnut Creek watershed near Ames, Iowa, to determine the chemical discharges, loads, and yields of nitrate-N, atrazine, and metolachlor. The total load and yield of nitrate-N in streamflow from a 2,540-ha subwatershed (site 310) of Walnut Creek from April 1991 to September 1992 was 150,000 kg and 58 kg/ha. Loads and yields of selected herbicides was 11,000 g and 4.5 g/ha for atrazine, and 19,000 g and 7.3 g/ha for metolachlor. Large chemical loads and increases in loads are closely related to periods of stormflow. Cumulative chemical loads were greater during the 1991 growing season, when soil conditions were wet and stormflow occurred shortly after application of chemicals, compared to the cumulative loads of chemicals during the 1992 growing season when stormflow did not occur until 2 months after application of chemicals. This was especially true for the herbicides. Nitrate-N is transported in significant quantities during periods of base flow at all times of the year.

<table>
<thead>
<tr>
<th>Site number (fig. 1) and type of flow evaluated</th>
<th>Nitrate-as-nitrogen yield (kilograms per hectare)</th>
<th>Atrazine yield (grams per hectare)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>July 16</td>
<td>August 5</td>
</tr>
<tr>
<td>310-Streamflow</td>
<td>0.51</td>
<td>0.11</td>
</tr>
<tr>
<td>220-Stormflow</td>
<td>0.003</td>
<td>0.003¹</td>
</tr>
<tr>
<td>220-Tileflow</td>
<td>0.49</td>
<td>0.11</td>
</tr>
<tr>
<td>110-Tileflow</td>
<td>0.51</td>
<td>0.09</td>
</tr>
</tbody>
</table>

¹July 15.
For July-August 1992, loads and yields in streamflow from the same subwatershed were 20,000 kg and 8.0 kg/ha for nitrate-N and 1,100 g and 0.42 g/ha for both atrazine and metolachlor. Loads and yields in stormflow from a 360-ha small basin (site 220) within the subwatershed were only 22 kg and 0.06 kg/ha for nitrate-N, 3.5 g and 0.010 g/ha for atrazine, and 2.6 g and 0.007 g/ha for metolachlor. Concurrent loads and yields in tileflow for the same small basin were 2,800 kg and 7.9 kg/ha for nitrate-N, 180 g and 0.50 g/ha for atrazine, and 130 g and 0.35 g/ha for metolachlor. On the basis of yields for this period of flow following 2 dry months, little of the chemical loads from the subwatershed appeared to have come from stormflow, whereas most of the loads appeared to have come from tileflow.

The tile lines draining this small basin do have a number of surface inlets, but the chemical loads from these inlets should be similar to those measured in the stormflow at the small basin outlet and should, therefore, have had little effect on the chemical loads and yields from the tile lines. Daily yields for July 16 (stormflow) and August 5 (base flow) compared to those from a 8.9-ha field-basin tile (site 110) with no surface inlets also indicates that tileflow is the primary transporter of agricultural chemicals for this period. Nitrate-N and atrazine yields were nearly identical for streamflow, tileflow with surface inlets, and tileflow without surface inlets, whereas yields for stormflow were much smaller.

REFERENCES CITED

Atrazine Transport Through Preferential Pathways at the Missouri MSEA

By James A. Tindall and William K. Vencill

Abstract

Results of experiments at the Missouri Management System Evaluation Area (MSEA) indicate that atrazine moved rapidly through the soil, probably due to the presence of a large number of cracks and macropores. Data also show that concentrations of atrazine exceeding 0.50 µg mL⁻¹ were observed with depth (45-135 cm) after several months following heavy recharge events. It appears that macropores were a major factor in atrazine transport at the site. Agriculture practices designed to reduce surface cracking (which will reduce access to macropores) and chemical input could play a major role in lessening contamination of ground water in the Midwest.

INTRODUCTION

Research and monitoring studies have shown widespread detection of various herbicides in shallow ground water in the midwestern United States as well as other locations (Hallberg, 1989). Both atrazine and alachlor, common postemergent herbicides used on corn, soybeans, and other field crops, have been detected in numerous states (U.S. Environmental Protection Agency, 1987). Residues of these two herbicides are commonly found in the Midwest and in California. Atrazine and alachlor concentrations as high as 10 µg L⁻¹ and 16 µg L⁻¹ respectively, have been reported in ground water in Iowa (Wintersteen and Hertzler, 1987). The processes of sorption, volatilization, degradation, persistence, mobility, and plant uptake, as well as the presence of preferential flowpaths interact over time to determine the fate and transport of herbicides. Environmental factors, such as evapotranspiration, precipitation, and temperature, also affect herbicide transport (Jury, 1986). There is convincing evidence that the presence of preferential pathways promotes rapid, deep movement of chemicals within agricultural soils (White, 1985; Edwards and others, 1990; Luxmoore and others, 1990).

Because non-point source (NPS) pollution has become a major water-quality concern in the United States, especially in the midcontinent area, five Management System Evaluation Areas (MSEA) have been established. These MSEA sites are located in Minnesota, Missouri, Iowa, Ohio, and Nebraska and have become part of the well known "midcontinent herbicide initiative." Research at these sites is being conducted through a collaborative effort with various universities, the U.S. Department of Agriculture-Agricultural Research Service, U.S. Environmental Protection Agency (USEPA), and U.S. Geological Survey. Because contamination of ground water by the major herbicides atrazine, alachlor, cyanazine, metolachlor, and metribuzin, as well as nitrate contamination from fertilizers have been found in these States, research at each MSEA site is focusing on the transport and transformation processes of these chemicals. Although it is well known that contamination by these compounds enters surface water and ground water through various pathways, the mechanisms by which they are transported are poorly understood. The research for this report was begun to determine how atrazine moves through the soil matrix, and the role of macropores in that movement through the clay soils at the Missouri MSEA.
MATERIALS AND EXPERIMENTAL METHODS

Six undisturbed experimental plots with a 1 m² surface area (two sets of three each) were instrumented in a fine montmorillonitic, mesic Udollic Ochraqualf Mollic albqualf, silty loam soil at the Missouri MSEA near Centralia in Boone County, Missouri, on May 11, 1991 (fig. 1). Three plots (plots 1 to 3) were 1.35 m deep, and the remaining three (plots 4 to 6) were 1.05 m deep. Zero-tension pan lysimeters were installed at 1.35 m in plots 1 to 3 and at 1.05 m in plots 4 to 6. Additionally, each plot was planted with soybeans (Glycine max L.) and instrumented with suction lysimeters and tensiometers at 15-cm increments. The tensiometers were automated with transducers attached to a data logger. Neutron-access tubes were installed in each plot and were read at 15-cm increments to determine moisture content. The zero-tension pan lysimeters (1 m²) was installed at the bottom of each plot without disturbing the soil above the pans. To accomplish this, the plots were excavated on the eastern and western sides and lined with 4-mil plastic to prevent lateral ground water flow through the plots. Plots were encased with a raised frame (8-cm high) to prevent any surface runoff (fig. 2). After installation, the plots were allowed to equilibrate for 1 year before data collection. During this waiting period, all suction and pan lysimeters were purged monthly and were sampled prior to herbicide application in May 1992. Initial atrazine concentrations were below detectable limits (0.05 μg/mL).

Figure 1. Site-location map.
The herbicide atrazine was applied on May 18, 1992 at a rate of 1.4 kg ha\(^{-1}\). Six hours after application, an infiltrometer was used to apply 5 cm of water to each plot (1.5 cm hr\(^{-1}\)). Water samples were extracted from suction and pan lysimeters monthly (June through November) and analyzed for atrazine on a high-precision liquid chromatograph (hplc) with a 25-mm by 4.6-mm column and an 80:20 volume-per-volume methanol-to-water ratio (adjusted to pH 7.4 with 0.05 M ammonium acetate). Wavelength was set at 222 nm with a retention time of 9.5 minutes and a flow rate of 8 mL minute\(^{-1}\). All samples were maintained at 0°C until analysis and filtered through a 0.45-m syringe filter prior to analysis. Atrazine concentrations were determined from standards and a linear regression curve (\(r^2 = 0.991\)). Standards as well as blank samples were inserted at frequent (blind) intervals to insure quality control. Soil samples also were extracted and analyzed by hplc. A 20-g sample of soil was cored from each depth increment, and atrazine was extracted by adding 42 mL of 90 percent methanol and 10 percent hplc-grade water, shaking for 2 hours, and centrifuging. The supernatant was collected, filtered, and analyzed.

**EXPERIMENTAL RESULTS AND DISCUSSION**

The zero-tension pan lysimeters were designed to intercept all water flowing vertically through each plot so that total flux (volume basis) could be determined. Concentrations of atrazine at depths of 60 to 135 cm (plot 1; fig. 3A) and 90 to 105 cm (plot 6; fig. 3B) 1 month after application are greater than would be expected if flow and chemical transport were through the soil matrix alone, because atrazine would normally be diffused within the soil matrix, allowing for little if any transport below 15- to 30-cm depths. Plots 1 and 6 (figs. 3A and 3B) were selected for illustration because they are representative of each of the six plots. In plots 4-6, the pan lysimeter was just below a claypan that exhibited severe cracking with slight decreases in water content (claypan cracks were observed on separate, adjacent plots). Cracking that was evident on the surface was likely caused by the development of cleavage planes at points of high-water content. As the soil dried, the cleavage planes separated, causing large cracks. Several surface cracks were 2 cm wide by about 20 m long; these cracks did not follow cultivation planes. Cracking of the claypan was probably the cause of the rapid transport of atrazine through the soil profile.
Figure 3. (A) Atrazine concentrations in ground water from suction and pan lysimeters (plot 1); and (B) Atrazine concentrations in ground water from suction and pan lysimeters (plot 6).

A companion laboratory study on undisturbed, unsaturated soil cores (28 cm diameter by 40 cm height) that were extracted by the method of Tindall and others (1992) and analyzed by the method of Green and others (1990), showed that the claypan, which is 40 to 80 cm below land surface, had anomalously high saturated hydraulic conductivity ($K_s$) values greater than 30 cm d$^{-1}$. After staining the cores in the laboratory study with crimson-red dye, large numbers of macropores were found in the claypan cores compared to cores collected from above and below the claypan, where $K_s$ averaged about 10 cm d$^{-1}$. Because of high clay content, $K_s$ values for claypan sediments are generally in the range of 3 to 4 orders of magnitude less than 30 cm d$^{-1}$. Thus, the high $K_s$ values are likely a result of the macroporosity of the claypan cleavage planes. Unsaturated hydraulic conductivities of the laboratory cores were in the same range as those which had been measured in the field plots ($10^{-1}$ to $10^{-3}$ cm d$^{-1}$) at the same relative water content ($\theta \approx 0.23$). Therefore, rapid transport of atrazine probably occurred under saturated conditions during times of large recharge events and, as the atrazine moved from the soil surface through the top 15-cm, it was able to move quickly through the claypan to the water table at a depth of about 1.5 m below land surface. The high $K_s$ values for the claypan probably account for the high peak concentrations of atrazine collected in the zero-tension pan lysimeters.

Generally, atrazine concentrations decreased with depth; however, large concentration peaks were observed at various depths and times within all plots. These peaks confirm that atrazine was being transported to a depth below 15 cm relatively quickly. Although the concentrations were lower with depth than those at the time of application, however, considerable amounts of atrazine were still being transported within the soil profile, as evidenced by the high peaks in August 16 samples (figs. 3A and 3B).

During the 6 month sampling period, 52-cm of rainfall was recorded. At the end of July 1992, the plots received about 15 cm rainfall just prior to the August 16 sampling. The atrazine concentrations in the 60- to 120-cm depth interval (fig. 3A) and 90- to 105-cm depth interval at plot 6 (fig. 3B) in August were much higher than atrazine concentrations near land surface. Prior to the November 22 sampling, about 7 cm of rainfall was recorded and similar, but smaller increases in atrazine concentration with depth occurred at the 90- and 135-cm depth interval at plot 1 (fig. 3A) and at the 90-cm and 105-cm depth interval at plot 6 (fig. 3B). High atrazine concentrations observed as late as August and November may reflect entrapment and partial desorption of atrazine from soil within the macropore system where it remained in immobile pockets until it was later flushed by recharging water.

Compared to concentrations in the water samples (fig. 4) extracted from the suction and pan lysimeters, the concentrations in the soil samples are greater near the surface but decrease with depth, as would be expected for bulk soil. At the surface (fig. 4), atrazine concentrations collected in cores in June are similar to applied concentrations, but soil samples collected in November indicate that large rainfall events caused fluctuations in atrazine concentrations in the soil matrix similar to fluctuations in the lysimeter extracts. The same trends are quite noticeable in soil and extract samples.

The difference in atrazine concentration in soil and extract samples at the 15-cm and other depths results from the fact that the suction lysimeters collect water that moves relatively quickly through the larger pores. As water and chemicals flow into the soil matrix, flow is retarded by the small size of the pores, which, because of capillary tension, restrict the flow of water to large conducting pores; because of these zones of restricted flow, some of the atrazine may be entrapped while additional amounts are adsorbed onto soil particles. Consequently, atrazine concentration in
the matrix is higher than can be sampled by the lysimeters, and each recharge event probably flushed the atrazine into the larger pores where it became much more mobile and was sampled later by suction lysimeters. With continual recharge and subsequent flushing during the growing season, atrazine concentrations in water from the suction lysimeters will gradually decrease to less than detectable limits, while concentrations will remain high within the soil matrix; accordingly, soil samples would represent the amount of atrazine stored in the soil. The results indicate that a portion of this soil stored atrazine may become available for transport and be flushed during large rainfall events.

**SUMMARY AND CONCLUSIONS**

Macropores are a major factor in transport of atrazine at the Missouri field site, where most of the macropores present are likely the result of cleavage plane separation. It appears that atrazine is not irreversibly adsorbed to the soils at this site and, during early stages of the growing season (within 1 to 2 months of application), it may subsequently leach after periods of heavy rainfall. Because large cracks and pores within the soil profile are at atmospheric potential, saturated or near saturated conditions are required for water to infiltrate the land surface in these areas. Consequently, a management system such as minimum tillage and normal tillage operations (this would not include no-till), that reduces surface cracking, thereby preventing chemical inputs from reaching macropores, could play a major role in lessening ground water contamination in this area. Also, the timing and frequency of application of the fertilizer or pesticide would be incorporated into a management strategy. Accordingly, management of current pesticide application practices may play a more important role than previously believed and, a mass-balance study of atrazine using 14C labeling would help quantify total amounts that may be reaching ground water.

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U.S. Geological Survey
Toxic Substances Hydrology Program--
Proceedings of the Technical Meeting,
Colorado Springs, Colorado,
September 20-24, 1993

By David W. Morganwalp and David A. Aronson

U.S. GEOLOGICAL SURVEY
WATER-RESOURCES INVESTIGATIONS REPORT 94-4015

Volume 2 of 2
The Toxic Substances Hydrology (Toxics) Program of the U.S. Geological Survey (USGS) provides earth-science information needed to prevent or mitigate contamination of the Nation’s ground-water and surface-water resources. The Toxics Program’s objective is to understand the movement and fate of toxic substances in the Nation’s ground water and surface water. The program’s research activities include (1) field and laboratory investigation of the physical, chemical, and biological processes that control the transport and fate of contaminants in ground water and surface water; (2) the development of new analytical methods and sampling techniques to measure the concentrations of toxic substances in water; and (3) the investigation of the relations among human activities, environmental characteristics, and regional patterns of water quality. Most of the research activities take place at contaminated sites. The major research objective is not characterization of contaminated sites, but is obtaining knowledge about contaminant-transport processes transferable to other contaminated sites. For example, the knowledge obtained at the research sites could be used to predict contaminant transport at other sites, improve methods for remediating contaminated ground water, design water-quality assessments, and identify potential causes of contamination.

Recent accomplishments of the Toxics Program have been presented at a series of technical meetings held in Tucson, Arizona (1984), Cape Cod, Massachusetts (1985), Denver, Colorado (1987), Pensacola, Florida (1987), Phoenix, Arizona (1988), and Monterey, California (1991). This report documents the oral and poster presentations given at the most recent meeting, held in Colorado Springs, Colorado, in September 1993. The sections in this report correspond to the topical organization of the meeting’s oral sessions. Each session focused on research at a specific contaminated site or on a topical subject. Papers associated with poster sessions were integrated into the appropriate section. The lead paper in most of the sections gives an overview of the research conducted at the site discussed.

Section A addresses the biodegradation of gasoline in ground water that resulted from a leaking underground storage tank in Galloway Township, New Jersey. The papers describe methods to determine in situ biodegradation rates of gasoline on the water table, the geochemistry of gasoline constituents dissolved in ground water, and air-flow modeling of gas transport in the unsaturated zone.

Section B describes fluid flow and solute transport in fractured rock at the Mirror Lake Site in New Hampshire, where methods to characterize contaminated fractured rock are being developed. The methods are interdisciplinary and draw on techniques from hydrology, geology, geochemistry, and geophysics. Specific examples of papers are (1) discussions on the use of well logs to help design tracer tests and (2) comparisons of subsurface fracture mapping with electromagnetic and seismic tomography and with borehole acoustic televiewer and borehole flowmeter logs.

Section C contains papers on the migration of sewage-contaminated ground water on Cape Cod, Massachusetts, and on the transport and fate of metals, microbes, and organic chemicals in ground water. The papers describe the use of a large array of multilevel samplers to conduct large- and small-scale (hundreds of meters to meters) tracer tests designed to study a variety of transport processes in ground water. Examples of topics of additional papers in this section include: phosphate contamination in ground water, the role of protozoa in an organically contaminated aquifer, and numerical simulation of contaminant transport.

Section D is on the biodegradation and transport of chlorinated solvents, such as trichloroethylene (TCE), in ground water at Picatinny Arsenal, New Jersey. The papers describe the desorption of TCE from aquifer sediments, the microbial degradation and transport of TCE in ground water, the volatilization and transport of TCE in the unsaturated zone, and the surfactant-enhanced remediation of ground water contaminated with TCE.

Section E presents the development of methods to analyze and collect water samples, and to investigate transport processes. These papers discuss, for example, the development of a new method to collect sediment cores without loss of sample, new analytical methods to measure the concentrations of pesticides and pesticide metabolites in water, and the use of nitrogen isotopes to study the subsurface transport of nitrogen.

Section F contains papers on the environmental fate of agricultural chemicals in the Midwest. The papers describe the occurrence, distribution, and transport of agricultural chemicals in ground water, streams, large rivers, reservoirs, and precipitation at
regional to test plot scales. Examples of specific topics in this section are papers on the relation of nitrate concentrations in surface water to land use, the persistence of herbicides in reservoirs, and the results of a reconnaissance of pesticides in near-surface aquifers. The final eight papers in this section present results from the Management Systems Evaluation Areas (MSEA) program, which is part of an interagency research program to evaluate the effects of agricultural-management (farming) systems on water quality.

Section G contains papers on the natural biodegradation and transport of crude oil in the subsurface at Bemidji, Minnesota. The papers describe crude-oil contamination that resulted from a pipeline failure. Because the time the contamination occurred and the amount of crude oil in the subsurface are known, this site has provided USGS researchers and others a unique opportunity to study contaminant hydrology; information on the source of contamination usually is not available for most sites of groundwater contamination. Examples of specific topics in this section are papers on the use of simulation to study field-scale solute transport and biodegradation, and on small-scale chemical heterogeneities in the contaminated aquifer.

Section H focuses on the fate of anthropogenic contaminants in the San Francisco Bay Estuary and tributaries in California. The papers describe the transport of pesticides from the San Joaquin and Sacramento Rivers, California, through the Sacramento-San Joaquin Delta, and into the Bay. In addition, the papers in this section describe the fate of organochlorine compounds, the results of a survey of molecular marker compounds, and the distribution and flux of sulfides in the Bay.

Section I contains papers on the transport and fate of toxic metals in acidic mine drainage in the headwaters of the Upper Arkansas River in Colorado. Results of tracer and pH-modification experiments in St. Kevin Gulch, Leadville, Colorado—a small mountain watershed—are discussed. These experiments were designed to isolate hydraulic transport processes so that geochemical processes can be studied.

Section J addresses a variety of topics relating to the hydrology of toxic substances in ground water and surface water. The papers are grouped by topic, and discuss, for example, the fate of organic compounds in surface water, the fate of hydrocarbons in the subsurface, the microbial degradation of explosive wastes, and the measurement of unsaturated-zone properties.

Section K reports on the transport of agricultural chemicals in ground water at an agricultural research plot near Plains, Georgia, where USGS and U.S. Department of Agriculture researchers collaborated on a tracer test involving bromide, atrazine, and other agricultural chemicals beneath a plot of irrigated corn. The papers discuss, for example, the two-dimensional distribution of a bromide tracer in the unsaturated zone, and the spatial variability of soil properties affecting the transport of agricultural chemicals.

Section L contains papers on nonpoint sources of groundwater contamination. These papers, which report results of studies on Long Island, New York, and the New Jersey coastal plain, describe the relation between land use and groundwater contamination.

Section M presents papers on acidic groundwater and surface-water contamination from copper mining near Pinal Creek, Arizona. The papers discuss, for example, the use of groundwater age dating to confirm estimates of travel times, the interaction of the contaminant plume with Pinal Creek, and the relations among algal species and chemical gradients in Pinal Creek.

Compiling and editing a proceedings of this size is a complex and difficult task. The task was made easier by the work and dedication of David Aronson, who died on April 7, 1996. David coedited two proceedings of technical meetings for the Toxic Substances Hydrology Program, and received awards for his work. This proceedings is a testament to his many contributions to the U.S. Geological Survey.

David W. Morganwalp
Acting Coordinator
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Evolution of the Contaminant Plume in an Aquifer Contaminated with Crude Oil, Bemidji, Minnesota

By Mary Jo Baedecker¹, Isabelle M. Cozzarelli¹, Philip C. Bennett², Robert P. Eganhouse¹, and Marc F. Hult³

Abstract

A long-term investigation of the geochemistry of a contaminant plume in an aquifer where crude oil floats on the water table indicates that the size of the plume of dissolved constituents has changed little over a 8-year period. Even though the geochemical reactions have changed over time and part of the plume has become anoxic, the biodegradation of dissolved hydrocarbons under oxic and anoxic conditions has prevented the hydrocarbons, in concentrations above Federal maximum contaminant levels, from moving more than 137 meters downgradient from the oil body. Another factor that helps contain the plume is the presence of silt layers of low hydraulic conductivity near the oil and the top of the saturated zone. The findings of this study support the conclusions that significant concentrations of petroleum-type hydrocarbons can be attenuated or removed from aquifers by natural hydrologic and biogeochemical processes.

INTRODUCTION AND OVERVIEW OF PROJECT

An investigation of the effects of a crude-oil spill on an aquifer was undertaken near Bemidji, Minnesota, as part of the Toxic Substances Hydrology Program of the U.S. Geological Survey (USGS). An underground pipeline carrying crude oil ruptured in 1979, and the oil sprayed over the land surface (referred to as the spray zone in fig. 1). After partial

Figure 1. Map of Crude-oil site near Bemidji, Minnesota, showing the location of the pipeline that ruptured, approximate location of the oil body, area over which oil was sprayed (spray zone), and locations of wells.

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removal of the product, about 410 m$^3$ of crude oil remained at the site (Hult, 1984). Some of the crude oil reached the ground water and is floating on the water table and a contaminant plume has developed in the aquifer downgradient from the oil body. A preliminary investigation and site characterization that began in 1983 was expanded in 1985 to examine (1) the fate of the crude oil, (2) development of the contaminant plume, (3) factors that affect the transport of chemical constituents, and (4) the effect of biogeochemical processes on aquifer solids. The scope of the work was expanded again in 1989 to investigate (5) the movement of the oil body, (6) partitioning at the oil/water interface, and (7) solute transport.

A summary of the major topics that have been investigated at the site is listed in table 1. The references are not inclusive and additional information can be found in publications referred to in the table and in USGS reports (see Mallard and Aronson, eds., 1991, for the most recent compilation of papers on this work). Many of the studies mentioned above are continuing and investigations are being expanded to include colloidal transport, sorption characteristics of the sediment, and microbial activity in the aquifer.

This paper describes the evolution of the contaminant plume and discusses the importance of assessing natural processes for removing petroleum-type hydro-

| Table 1. Topics of investigation and selected references for research at the Bemidji, Minnesota site from 1984-93 |

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carbons from ground water. The geochemistry of the plume has been examined in detail for a 8-year period to document the changes in the aquifer caused by the alterations and transport of hydrocarbons.

**DESCRIPTION OF SITE AND METHODS**

The study site is located in the Bagley outwash plain Bemidji, Minnesota. The surficial aquifer is about 20 m thick and consists of sand and gravel outwash overlying till. Thin, discontinuous silt layers are interbedded with sand near the water table (Franzi, 1988). The water table, in the part of the aquifer studied in this report, is 6 to 10 m below land surface. Only the upper 5 to 8 m of the aquifer has been affected by crude oil. Locally ground water flows to the northeast and discharges to a small lake. The average linear flow velocity of water in the aquifer is 0.1 to 0.5 m/d, but velocities as low as 0.05 m/d were measured in the fine-grained silty material (Bennett and others, 1993). The aquifer is mostly quartz with 30 percent feldspar, 5 percent carbonate, and less than 5 percent clay minerals (Bennett and others, 1993).

Piezometers were installed by hollow-stem auger and the wells were screened in depth intervals of 0.15, 0.61 or 1.52 m. The screens were stainless steel and the casings were polyvinyl chloride. Water samples were collected with submersible pumps for analyses of inorganic constituents and dissolved organic carbon and with a Teflon bailer for analyses of organic constituents. Methods of chemical analyses presented in this paper are found in Eganhouse and others (1993) for hydrocarbons; in Baedecker and Cozzarelli (1992) for dissolved oxygen (DO), ferrous iron (Fe$^{2+}$), volatile dissolved organic carbon (VDOC), methane (CH$_4$) and carbon isotopes; and in Baedecker and others (1993) for other analytical methods and field sampling methods.

**DEVELOPMENT OF THE CONTAMINANT PLUME**

Plume development depends primarily on aquifer transmissivity, the extent of volatilization and solubilization of the contaminants, the amount of sorption, and the degradability of the dissolved constituents. The main components of crude oil at the Bemidji site are normal, alicyclic, and aromatic hydrocarbons. The most soluble aromatic hydrocarbons, benzene and the alkylbenzenes, are known to degrade by microbial processes (Atlas, 1984). When the plume developed shortly after the spill, concentrations of oxygen present in the aquifer were sufficient to oxidize the hydrocarbons by aerobic microbial processes. After oxygen was depleted, the major processes that oxidized hydrocarbons in the anoxic zone were iron and manganese reduction and methanogenesis (Baedecker and others, 1989, 1993). It was demonstrated that these processes are linked with hydrocarbon oxidation in laboratory experiments using pure cultures for iron reduction (Lovely and others, 1989) and mixed cultures for methanogenesis (Grbic-Galic and Vogel, 1987). Aerobic oxidation of hydrocarbons continues to be a major process at the edges of the anoxic zone where hydrocarbons come in contact with oxygenated ground water.

The plume at the Bemidji site can be defined by the distributions of VDOC; specific hydrocarbons (Eganhouse and others, 1993); geochemical indicators such as pH and DO (Baedecker and others, 1993); and inorganic solutes such as calcium (Bennett and others, 1993). The distributions of DO, VDOC, and Fe$^{2+}$ in 1987 and 1992 are shown in fig. 2. Oxygenated ground water moved upward in the middle of the anoxic zone in 1992. Concentrations of DO ranged from 0.05 to 2.4 mg/L in a 4-m-thick zone below the top of the saturated zone that extended 70 m downgradient from the anoxic zone. These concentrations were less than background DO concentrations of 8 mg/L. The distributions of VDOC were similar in 1987 and 1992 as shown in fig. 2, but the zone having VDOC concentrations greater than 10 mg/L has become smaller, the plume has become less contaminated in the middle, and it is sinking at the leading edge. A major change from 1987 to 1992 was observed for the leading edge of the 10 mg/L contour of the Fe$^{2+}$ plume which has moved downgradient at a rate of about 6 m/yr.

The change over 8 years (1984-1992) in the chemical composition of the plume near the oil body is shown in fig. 3 for Mn$^{2+}$, Fe$^{2+}$, CH$_4$, and the $\delta^{13}$C of the total inorganic carbon. The data are for a sampling point in the plume at the downgradient edge of the oil (location 533 on fig. 1), and the screened interval is about 1 m thick at the water table. These results indicate that Mn(IV) reduction preceded Fe(III) reduction and methanogenesis (Baedecker and others, 1993). The change in measurements of the total inorganic carbon toward heavier numbers over time is due to the
Figure 2. Hydrologic sections (A-A’ in fig. 1) of the contaminant plume showing the anoxic zone, and distribution of volatile dissolved organic carbon and ferrous iron in 1987 and 1992. The water table is 6 to 10 meters below land surface.
formation of methane. Concentrations of Mn$^{2+}$ increased to 0.12 mM and then decreased to 0.01 mM, whereas Fe concentrations increased by a factor of 30 to 0.92 mM, and concentrations of CH$_4$ increased from the detection limit (0.006 mM) to 1 mM (fig. 3). Concentrations of both Fe$^{2+}$ and CH$_4$ have decreased slightly in recent years. The data indicate that Mn(IV) reduction has become a less important reaction over time near the oil body. The data suggest that both Fe(III) reduction and methanogenesis continue to be major reactions in the anoxic plume.

Concentrations of total benzene and alkylbenzenes in ground water were 10.4 to 18.4 mg/L, respectively, at three sampling locations within 1 meter of the oil body (1990 and 1992 data). Concentrations of hydrocarbons in the ground water varied over time and spatially near the oil body, probably because small oil stringers were associated with the sediment near the source. Oil stringers on a scale of millimeter to a few centimeters were observed in sediment cores obtained downgradient from the oil body. Also, ground water pumped near the oil body had an oily sheen even where a separate fluid phase was not encountered.

At location 518 (fig. 1), 56 m downgradient from the middle of the oil body, concentrations of benzene and alkylbenzenes were more consistent over a 5-year period (fig. 4) than they were at locations close to the oil body. Benzene was the major hydrocarbon present, and its concentration decreased over time, whereas concentrations of the other hydrocarbons were low but increased over time. Concentrations of toluene were equal to or less than 0.007 mg/L and concentrations of the xylenes, the C$_3$-benzenes and the C$_4$-benzenes were equal to or less than 0.35 mg/L. At locations beyond 137 m the oil body, concentrations of hydrocarbons were less than Federal drinking water standards.

DISCUSSION AND CONCLUSIONS

Although the geochemical processes have changed over time, the plume has not migrated as far as predicted considering the ground water flow velocities and sorption constants for these compounds (Baedecker and others, 1993). A factor that may affect migration of contaminated ground water is the presence of discontinuous silt layers (Franzi, 1988; Baehr and Hult, 1991) that have low hydraulic conductivity. Thus, the flow velocities in these zones may be low and retard the movement of fluids. However, the primary reason that the anoxic plume has not farther and that only trace concentrations of hydrocarbons are found in ground water farther than 137 m...
downgradient from the plume is that the hydrocarbons have biodegraded under oxic and anoxic conditions. The rate of removal of organic contaminants by natural biodegradative processes and the factors that affect these rates are important considerations in making decisions concerning cleanup of contaminated ground water. Biodegradation of petroleum-derived hydrocarbons in aerobic and sub-oxic environments is generally considered a more efficient attenuation mechanism than is biodegradation in anoxic environments. However, biodegradation in anaerobic environments also may remove significant amounts of hydrocarbons from ground water. Estimated half-lives of benzene, toluene, and the xylenes in methanogenic field sites were 0.5 to 3.8 years at five sites (Barker and Wilson, 1992). Natural processes may account for the removal of significant quantities of petroleum hydrocarbons in the subsurface. Additional work needs to be done to determine ground-water flow velocities and rates of intrinsic degradation on small scales in contaminated aquifers to evaluate natural processes as part of long-term remedial action programs.

REFERENCES


Use of Simulation to Study Field-Scale Solute Transport and Biodegradation at the Bemidji, Minnesota, Crude-Oil Spill Site

By H.I. Essaid¹, M.J. Baedecker², and I.M. Cozzarelli²

Abstract

A two-dimensional, multispecies solute-transport model that includes aerobic and anaerobic degradation processes was developed and applied to the Bemidji, Minnesota, crude-oil spill site. The model was used as a tool to study the field-scale solute-transport and degradation processes. The simulations included the transport of degradable and refractory dissolved organic carbon, dissolved oxygen, and methane, as well as aerobic and anaerobic (methanogenic) biodegradation. Despite the considerable uncertainty in the model parameter estimates, results of simulations reproduced the general features of the observed ground-water plume. In addition to the kinetics of the biodegradation processes, important factors that affect the distribution of the solutes in the field are the recharge influx and the degree of dispersion and mixing in the ground water system. Recharge influx causes flow lines in the aquifer to be deflected downward from the water table causing downward movement of the plume. Biodegradation results in a narrow plume with sharp gradients at the margins. Spatial variability of hydraulic conductivity increases the amount of carbon degraded by aerobic and anaerobic processes.

INTRODUCTION

Numerous researchers working at the Bemidji, Minn. crude-oil spill site (fig. 1) have documented evidence for microbial degradation of petroleum hydrocarbons in the field. Chang and others (1991) studied the kinetics of aerobic crude-oil biodegradation in laboratory microcosms using materials from the site. Methanogenesis has been observed in the unsaturated (Hult and others, 1991) and saturated zones (Bennett and others, 1993; Eganhouse and others, 1993; Baedecker and others, 1993). Cozzarelli and others (1990) identified organic acids produced by oxidation of monoaromatic hydrocarbons by anaerobic degradation processes, and Lovley and others (1989) showed that Fe(III)-reducing organisms can oxidize an aromatic hydrocarbon anaerobically. Hiebert and Bennett (1992) used in-situ microcosms to study the accelerated chemical weathering of silicates by surface-adhering bacteria.

As a result of these studies, five geochemical zones in ground water (fig. 2) have been identified at the crude-oil spill site (Baedecker and others, 1989; Baedecker and others, 1993; and Bennett and others, 1993). Zone 1 consists of oxygenated uncontaminated native ground water. Zone 2, which is below the area where the land surface was sprayed by oil following the pipeline rupture, is characterized by reduced oxygen concentrations and the presence of refractory high molecular-weight hydrocarbons. Zone 3, beneath and immediately down gradient from the separate-phase oil lens, consists of an anoxic plume of ground-water that contains high concentrations of hydrocarbons and methane. Zone 4 is the transition zone from anoxic conditions to fully oxygenated conditions, and concentrations of hydrocarbons decrease rapidly as a result of aerobic degradation processes.

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Zone 5 consists of oxygenated water downgradient of the contamination plume that contains slightly elevated concentrations of dissolved constituents. Long-term monitoring of the plume since 1984 has shown that, near the water table, the concentration of total dissolved organic carbon (TDOC) and dissolved oxygen (DO) downgradient from the oil lens has remained relatively stable with time. In the anoxic zone (Zone 3) concentrations of reduced manganese (Mn) and iron (Fe), and methane have increased with time, indicating a sequence of Mn reduction followed by Fe reduction and methanogenesis.

In this study, a two-dimensional, multispecies solute-transport model that incorporates biodegradation was developed and applied to the ground-water system at the Bemidji, Minn. crude-oil spill site. The model was used as a tool to study the subsurface solute-transport and degradation processes. The goal of this study is to use the model to quantify the field-scale degradation processes and to identify the important factors affecting the distribution of solute species in the field. This report describes the preliminary results of the solute-transport and biodegradation modeling at the Bemidji, Minn. site.
THE NUMERICAL MODEL

A numerical model was developed to simulate the aerobic and anaerobic degradation processes that have been observed in the contaminated ground-water plume at the spill site. The model was used as a tool to study the physical, chemical, and microbial processes affecting the transport of dissolved species. Steep concentration gradients observed in the field data required that the model be capable of handling sharp fronts without introducing numerical dispersion. For this reason, the U.S. Geological Survey’s Method of Characteristics transport model (Konikow and Bredehoeft, 1978, Goode and Konikow, 1989) was expanded to handle multiple solutes and to include biodegradation terms. The approach of Kindred and Celia (1989) was used to represent the biodegradation terms in the transport equation as outlined below.

The two-dimensional transport equation solved in the model for each solute species includes linear sorption and biodegradation assuming a uniform porosity and fluid density as follows:

$$\frac{\partial C_i}{\partial t} = \frac{1}{b} \frac{\partial}{\partial x_j} \left( b D_{jk} \frac{\partial C_i}{\partial x_k} \right) - V_j \frac{\partial}{\partial x_j} C_i + \frac{W(C_i - C_i^*)}{(\varepsilon b)} - K_d C_i - K_c C_i \ , \quad (1)$$

where $C_i$ is the concentration of the $i$th solute, $R_i$ is the retardation factor for the $i$th solute, $t$ is time, $b$ is the width of the vertical cross-section through the aquifer, $D_{jk}$ is the dispersion tensor, $x_j$ and $x_k$ are the spatial coordinates, $V_j$ is the average linear velocity of the fluid, $W$ is the source fluid flux, $\varepsilon$ is the porosity, $C_i^*$ is the concentration of the $i$th solute in the source fluid, $K_d$ is the first-order biodegradation reaction term, and $K_c$ is the zero-order biodegradation reaction term.

Michaelis-Menton uptake kinetics is used to represent the degradation process, whereby

$$v^o_i = \frac{\frac{V_m^o}{K_h^o} C_i}{\frac{V_m^o}{K_h^o} + C_i} \ , \quad (2)$$

where $v^o_i$ is the specific uptake rate of solute $i$ by microbial population $n$, $V_m^o$ is the asymptotic maximum specific uptake rate, and $K_h^o$ is the half-saturation constant. The total uptake of solute $i$ is simply equal to the specific uptake rate multiplied by the biomass of population $n$. As can be observed by examining equation 2, when $C_i$ is large, $v^o_i \approx \frac{V_m^o}{K_h^o}$ is of zero order, and when $C_i$ is small, $v^o_i \approx \frac{V_m^o}{K_h^o} C_i$ is of first order.

As outlined by Kindred and Celia (1989) the biodegradation terms in equation 1 can be represented as follows. If degradation is substrate limited, the first order degradation term is given by

$$K_d = \sum_n \frac{V_m^o X^n}{K_h^o^n I_c + C_i} \ , \quad (3)$$

where $X^n$ is the biomass concentration of microbial population $n$, $I_c$ and $I_h$ are the biomass and competitive inhibition factors, respectively, given by $I_i = 1 + \frac{Q_i}{k_i}$

where $Q_i$ is the concentration of the inhibiting substrate $i$, and $k_i$ is the inhibition constant for that substance. The zero-order degradation term is given by:

$$K_c = \sum_n \frac{\gamma^n_i K_i - \sum_p \gamma^n_p K_p - \sum_n \frac{1}{\gamma^n_p k^n_p X^n}}{\gamma^n_i k^n_i X^n} \ , \quad (4)$$

where $\gamma^n_i$ is the cell-yield coefficient of the limiting substrate $i$, $\gamma^n_p$ is the cell-yield coefficient of substrate $i$, $K_i$ is the total uptake of the limiting substrate, $\gamma^n_p$ is the $i$-$p$ reaction ratio, $K_p$ is the total amount of parent compound $p$ metabolized, and $k^n_m$ is the death rate or maintenance constant. The terms on the right hand side of equation 4 represent, respectively, the zero-order uptake of substrate $i$, the production of substrate $i$ by metabolism of a parent compound, and release of substrate $i$ because of cell death.

The rate of biomass growth is given by:

$$\frac{dX^n}{dt} = \left( \gamma^n_i K_d C_i - k^n_m \right) X^n \ .$$

The model solves the ground-water-flow equation and then uses the velocities obtained from the flow solution to compute the movement of particles through the system. A separate set of particles is used for each solute in order to allow for different retardation factors. The degradation terms $K_d$ and $K_c$ are calculated explicitly at the end of each time step. The amount of biomass is then calculated using the integral of equation 5.
Figure 2. The simulated section showing ground-water zones 1 through 5 of the contaminated ground-water plume and simulated recharge zones A through E. (Modified from Baedecker and others, 1989. fig. A-6.)

For one-dimensional test cases, the results of this model compared favorably to results of the model of Kindred and Celia (1989).

SIMULATION OF THE OBSERVED PLUME

A two-dimensional cross-section was designed to simulate the observed contaminated ground-water plume at the Bemidji, Minn. site. The section is approximately parallel to the direction of ground-water flow. Ground-water samples from numerous wells along this section have been analyzed over time (Baedecker and others, 1993; Bennett and others, 1993; Eganhouse and others, 1993). The locations of the midpoints of the screened intervals of the wells that have been sampled are shown in figure 2. Water table wells were installed with a 1.52-m screen length and deeper sampling wells with 0.15 or 0.61-m screen lengths.

A vertical cross-section of unit width approximating the sampling transect was simulated using the transport model for the period from the time of the spill in 1979 until September 1990. Steady-state flow, no sorption, and isothermal conditions were assumed; the decrease in aquifer thickness caused by the change in water-table elevation was neglected. Four solutes and two microbial populations were modeled. Total dissolved organic carbon (TDOC) was split into two fractions—degradable dissolved organic carbon (DDOC) and refractory dissolved organic carbon (RDOC). The remaining two solutes modeled were dissolved oxygen (DO) and methane. To represent the aerobic and anaerobic degradation processes, aerobic and methanogenic populations of bacteria were included in the simulations. Iron and manganese reductions were not included because of the complexity of incorporating the rock-water interactions of dissolution and precipitation in the transport model.

For simulation purposes, the system was represented by an initially clean aquifer with background dissolved organic carbon concentrations and fully oxygenated water. Following the oil spill, DDOC and RDOC dissolved and entered the aquifer with recharge water. In the spray zone, we assumed that the major fraction of carbon entering the aquifer was refractory, whereas in the immediate zone of the oil body, we assumed most carbon was degradable. Hult and others (1991) have shown that biodegradation above the water table depletes the oxygen resulting in an anoxic unsaturated zone in the vicinity of the oil. Therefore, it was assumed that there was no oxygen in the recharge water near the oil body, and that oxygen was partially depleted in the recharge water in the spray zone. Competitive inhibition was used to represent the suppression of methanogenesis by oxygen. In this manner, as oxygen in the ground water is consumed and an anoxic zone develops, the methanogens begin to flourish resulting in increased methane production.

The simulated section is shown in figure 2. The oil present in the pore space within the oil body makes it difficult for water to flow through this zone. The magnitude of reduction of water flow is a complex function of the oil distribution. As a first approximation of this effect, the hydraulic conductivity and
recharge rate were reduced to 25 percent of the aquifer values in the zone of the oil body. Constant heads of 424.0 m and 422.6 m were specified at the upgradient and downgradient lateral boundaries, respectively. The bottom boundary condition was no flow, and a constant rate of recharge was specified across the top of the aquifer. The estimated values of initial concentrations and recharge water concentrations for each solute are given in table 1. The parameter values used in the simulation are given in table 2. There is considerable uncertainty in the values of the model parameters. Estimates of permeability (Essaid and others, 1991; Dillard and others, 1996) and measurements of velocity (White, 1991) have been made at the site; however, the values range over several orders of magnitude. No measurements or estimates are available for the transport and biodegradation parameters under the natural field conditions. Therefore, reasonable estimates of these values were used in the simulations.

Table 1. Initial and recharge water concentration in milligrams per liter

<table>
<thead>
<tr>
<th>Solute</th>
<th>Initial Concentration</th>
<th>Recharge Zone</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td>DDOC</td>
<td>0.0</td>
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<tr>
<td>RDOC</td>
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<td>2.0</td>
</tr>
<tr>
<td>DO</td>
<td>9.0</td>
<td>9.0</td>
</tr>
<tr>
<td>Methane</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

RESULTS AND DISCUSSION

Observed and simulated profiles of TDOC, DO, and methane near the water table are plotted in figure 3. Measurements in wells near the water table and immediately below the oil body were used for comparison. The screen length of most wells is 1.52 m; approximately half of the screen is below the water table. To approximate the measured values, the simulated values near the water table were calculated by averaging the concentrations of the first 0.8 m below the top of the simulated section.

The concentration profile of TDOC is shown in fig. 3a. The observed points show a concentration distribution at the water table that is relatively stable with time. The simulation has captured this feature as can be seen by the similarity between the simulated 1986 and 1990 concentration profiles. There is an increase in TDOC concentration in the upgradient spray zone, followed by a rapid increase in TDOC concentration in the zone of the oil body.

Table 2. Parameters used in the transport model simulation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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<tr>
<td>X-direction grid spacing</td>
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<tr>
<td>Y-direction grid spacing</td>
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<tr>
<td>Porosity</td>
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<td>Hydraulic conductivity</td>
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<td>Average linear velocity</td>
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<tr>
<td>Recharge</td>
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<tr>
<td>Longitudinal dispersivity</td>
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<td>Transverse dispersivity</td>
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</table>

Biodegradation Parameters:

<table>
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<tr>
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<th>Value</th>
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</thead>
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<tr>
<td>V(_m)</td>
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<tr>
<td>K(_h)</td>
<td>0.09 mg/L</td>
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<tr>
<td>Y</td>
<td>0.21 L/mg</td>
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<tr>
<td>Aerobic consumption of DO:</td>
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<td>V(_m)</td>
<td>0.99 /d</td>
</tr>
<tr>
<td>K(_h)</td>
<td>0.14 mg/L</td>
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<tr>
<td>Y</td>
<td>0.08 L/mg</td>
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<tr>
<td>Anaerobic degradation of DOC (methanogenesis):</td>
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</tr>
<tr>
<td>V(_m)</td>
<td>0.25 /d</td>
</tr>
<tr>
<td>K(_h)</td>
<td>0.06 mg/L</td>
</tr>
<tr>
<td>Y</td>
<td>0.06 L/mg</td>
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<tr>
<td>Biomass inhibition constant (I(_n))</td>
<td>1.0 mg/L</td>
</tr>
<tr>
<td>Methanogenesis inhibition constant (I(_m))</td>
<td>0.005 mg/L</td>
</tr>
</tbody>
</table>

Downgradient from the oil body, the TDOC concentration decreases gradually to the background concentration. This decrease is a result of microbial and physical processes. First, there is the anaerobic degradation of DDOC within the anoxic zone near the oil body and aerobic degradation of DDOC as it moves away from the oil body and encounters oxygenated recharge water (fig. 3b). However, even the concentration of refractory DOC (fig. 3c) decreases to background levels and achieves a steady-state profile near the water table. This is a result of the physical processes of displacement and mixing of flowing ground water with recharge water.
Figure 3. Graphs showing the observed and simulated concentrations near the water table for (a) total dissolved organic carbon (TDOC), (b) degradable dissolved organic carbon (DDOC), (c) refractory dissolved organic carbon (RDOC), (d) dissolved oxygen (DO), and (e) methane. The x-axis is distance along the simulated section in meters.
The dissolved oxygen concentration profile (fig. 3d) decreases in the spray zone because of the decrease in DO concentration in recharge water (assumed to occur because of degradation of hydrocarbons in the unsaturated zone) and the consumption of oxygen by degradation in the ground water. Near the oil body and immediately downgradient from it, the DO of the recharge water is assumed to have been completely consumed in the unsaturated zone. An anoxic zone develops in this area. However, DO begins to increase as oxygenated recharge water enters the system farther downgradient.

Methane is produced in the anoxic zone that develops in the immediate vicinity and downgradient of the oil body. The methane peak is displaced downgradient from the center of the oil body because of the input of methane-free ground water from the upgradient area. The decline in methane concentration at a distance of 230 m (fig. 3e) is a result of the upwelling of oxygenated water caused by the upward bending of flow lines around the less water-permeable oil body as the oil body decreases in thickness. The simulated profiles show a marked increase in methane production from 1986 to 1990 as population of methanogens increases. This increase in methanogenesis results in a slight decrease in DDOC concentrations from 1986 to 1990 (fig. 3b).

In order to examine the effect of degradation on DDOC in the aquifer, two-dimensional distributions of DDOC for three different simulations are shown in figure 4. In the first simulation, there is no degradation (fig. 4a); in the second simulation (described above) degradation occurs (fig. 4b); and in the third simulation degradation occurs and the hydraulic conductivity distribution is heterogeneous (fig. 4c). The distribution of DDOC for the case with no degradation (fig. 4a) reflects the physical processes of dispersion, diversion of flow around the oil body because of its reduced water hydraulic conductivity, and the depression of the plume beneath the water table because of the deflection of flow lines by incoming recharge water.

In the second simulation, the anaerobic and aerobic degradation processes result in a contaminant plume that is narrower than the plume in the first simulation and whose concentration gradients are comparatively sharp at the edges (fig. 4b). In this simulation, 46 percent of the total DDOC mass entering the aquifer is degraded--14 percent by anaerobic degradation and 32 percent by aerobic degradation. Previous work has shown that the hydraulic properties of the aquifer are spatially variable (Essaid and others, 1991; Essaid and others, 1993; Dillard and others, 1996). To make the simulation more realistic, a heterogeneous hydraulic conductivity distribution was created using the methods of Dillard and others (1996) and was used in the transport model. Because of the complex flow field, an irregularly shaped plume develops (fig. 4c). The average linear velocities of ground water (Darcy velocity divided by porosity) in this simulation range from $3.0 \times 10^{-10}$ to 1.6 m/d, with a mean of 0.13 m/d. The variability in flow paths and flow velocities results in increased mixing and dispersion of ground water. This, in turn, results in increased biodegradation. Of the total DDOC mass entering the aquifer, 60 percent is degraded--21 percent by anaerobic degradation and 39 percent by aerobic degradation.

The simulations presented in this paper represent a highly simplified representation of the true field conditions and neglect Fe and Mn reduction. Also, the parameters used in the simulations are highly uncertain. Nevertheless, the results do reproduce the general features of the observed contaminated ground water plume. In addition to the kinetics of the biodegradation processes, important factors that affect the magnitude of degradation and the distribution of the solutes in the field are the recharge influx and the degree of dispersion and mixing in the ground water system.

SUMMARY

A two-dimensional, multispecies solute-transport model that includes aerobic and anaerobic degradation processes was developed and applied to the Bemidji, Minn., crude-oil-spill site. The model was used as a tool to study field-scale solute transport and degradation processes. Simulation results indicate that, in addition to the kinetics of the biodegradation processes, important factors that affect the distribution of the solutes in the field are the recharge influx and the degree of dispersion and mixing in the ground-water system. Recharge influx deflects flow lines in the aquifer downward from the water table causing downward movement of the plume. Biodegradation produces a narrow plume with sharp gradients at the margins. Spatial variability of hydraulic conductivity increases the amount of carbon degraded by aerobic and anaerobic processes.
Figure 4. Sections showing the simulated distribution of degradable dissolved organic carbon with (a) no biodegradation, (b) biodegradation, (c) biodegradation and a heterogeneous distribution of hydraulic conductivity.
REFERENCES


Source Mass Balance Calculated from Changes in Composition of Spilled Crude Oil in the Subsurface near Bemidji, Minnesota

By Matthew K. Landon¹ and Marc F. Hult¹

Abstract

The transport and fate of crude oil that spilled from a break in a buried pipeline near Bemidji, Minnesota, on August 20, 1979, has been monitored by the U.S. Geological Survey since 1983. The oil percolated to the water table in a glacial outwash aquifer. The oil has moved about 30 meters as a separate fluid phase in the aquifer and is preferentially losing soluble and volatile compounds through dissolution into ground water and vaporization into the unsaturated zone. As part of the research effort at the site, the evolution of the composition and physical properties of the oil in the subsurface was studied. The primary objectives were to (1) quantify changes in the composition and physical properties of the oil at the site, (2) compare field results with oil alteration under controlled laboratory conditions that simulated the field environment, and (3) estimate mass balances for the total oil and for individual compounds mobilized during natural alteration of the oil source.

Analysis of oil collected from monitoring wells screened in the oil bodies during 1988 and 1989 indicated that areal differences in the physical properties of the oil have developed because of spatially and temporally variable rates of alteration of the originally uniform oil. The composition of the oil fraction lighter (with a lower carbon number) than dodecane (a normal alkane with 12 carbon atoms) of field and laboratory aged samples of oil was determined using gas chromatography/mass spectroscopy (GC/MS).

The oil has selectively lost aromatic compounds and aliphatic compounds (normal, branched, and cyclic alkanes) more volatile than nonane (normal alkane with nine carbons). About 50 detectable compounds have been depleted in the fraction of the oil that was analyzed. Maximum depletions of the total mass of C3 (compounds with three carbons), C4, C5, C6, C7, C8, C9, and C10 compounds were 100, 100, 95, 81, 66, 48, 49, and 25 percent, respectively. Depletion of the total mass of aromatic compounds ranged from 30 to 84 percent and exceeded depletion of the total mass of aliphatic compounds, which ranged from 0 to 73 percent. The greater depletion of aromatic compounds may indicate that dissolution of aromatic compounds into water initially occurs at greater rates than losses of aliphatic compounds by volatilization. Because of the much greater abundance of aliphatic compounds in the oil, however, more than 70 percent of the mass loss from the oil likely occurs as a result of volatilization. Losses of C6 and C7 aliphatic compounds account for a majority of the total loss of mass from the oil. Total mass loss from the oil calculated from changes in oil composition agrees within 0 to 3.8 percent (median of 1.6 percent) to mass loss calculated from changes in specific gravity, refractive index, and kinematic viscosity, indicating that any of these properties can be used for mass-balance calculations. Minimum estimates of total mass loss from the oil based on changes in composition and physical properties range from 0 to 11 percent (average is 3.8 percent) since the spill occurred in 1979. The results of mass loss calculations provide an independent estimate of the spatially variable source term for transport models of volatile and soluble hydrocarbons emanating from the oil source in the subsurface.

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INTRODUCTION

The composition and physical properties of spilled crude oil in a shallow subsurface environment change because of vaporization of volatile organic compounds into the unsaturated zone, dissolution of soluble organic compounds into ground water, and soil moisture, and biodegradation. The potency of a body of spilled petroleum as a source of environmental contamination, therefore, can change with time because of natural alteration processes.

Research to quantify changes in the composition and physical properties of spilled crude oil in the shallow subsurface in an undisturbed setting was conducted at a site near Bemidji Minn. (fig. 1). A description of the site was given by Hult (1984). This study is part of an interdisciplinary, long-term research effort at the Bemidji site to improve understanding of the mobilization, transport, and fate of petroleum contaminants in the shallow subsurface (Hult, 1991). The objectives of this study are to (1) quantify changes in composition and physical properties of the oil at the site, (2) compare field results with oil alteration under controlled laboratory conditions that simulate the field environment, and (3) estimate mass balances for the total oil and for individual compounds mobilized during natural alteration of the oil source. This paper presents measurements of oil composition and calculations of mass loss from the oil on the basis of changes in composition. Measurements of physical properties and calculations of mass loss from the oil in the field using laboratory relations between changes in physical properties and mass loss were presented in Landon and Hult (1991).

METHODOLOGY

Oil was collected from 14 wells during July 1988 and from 17 wells during June 1989. Each well was completed with a 5-cm inside-diameter (i.d.) 1.5-m-long stainless-steel screen. The samples were collected with a Teflon bailer, placed in airtight glass containers to prevent loss of volatile constituents, and stored at approximately 5 °C until analysis. The oil samples that were collected represented vertically integrated composites of the oil in the vicinity of the well screen over the length of the screen. Analysis of oil samples collected 24 hrs after initial sampling indicated that the oil collected from the wells had the same physical properties as oil that seeped in from the surrounding aquifer material; the oil samples collected from the wells were, therefore, representative of oil in the subsurface.

Figure 1. Location of Bemidji, Minn., research site and areal map of monitoring wells sampled for crude oil in July 1988 and June 1989.

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The kinematic viscosity, specific gravity, and refractive index of oil samples collected in the field were measured at 7.5 °C—the approximate mean annual ground-water temperature at the Bemidji site (Landon and Hult, 1991). Split samples of the oil collected in the field were allowed to volatilize inside a chamber at 7.5 °C to simulate oil alteration by vaporization under subsurface conditions and to determine relations among mass loss and changes in physical properties (Landon and Hult, 1991).

Gas chromatography/mass spectroscopy (GC/MS) was used to analyze the composition of the oil fraction lighter (with a lower carbon number) than dodecane (a normal alkane with 12 carbon atoms) in 13 samples collected in the field in 1989, and in three sets of samples from the laboratory aging experiments. Because the oil fraction lighter than dodecane contains the hydrocarbons that have the greatest vapor pressures and aqueous solubilities, this fraction is most likely to undergo changes in composition and loss of mass. Measurements of loss of mass from this lightest fraction of the oil are likely to account for the large majority of the total loss of mass from the oil, because the heavier fractions of the crude oil (with larger carbon numbers than dodecane) contain hydrocarbons with smaller vapor pressures and solubilities.

One part of oil was dissolved in 33 parts dodecane. The oil-dodecane mixtures were thoroughly mixed, and 1-mL samples were extracted and injected into a GC attached to a mass selective detector. A 60-m length of a DB-1, 0.325-mm i.d., fused-silica capillary column with a 5.0-μm film thickness was used in the GC. Helium was used as the carrier gas with a flow rate of 1 mL/min at 40 °C. The oven temperature of the GC was held at 40 °C for 5 minutes after injection and then the temperature was raised at a rate of 2 °C per minute from 40 to 200 °C from 5 to 85 min after injection.

Standards were analyzed to establish the retention times and retention order of major compounds and to compare the mass spectral characteristics of known compounds to sample peaks to facilitate compound identification. The relation between peak area and concentration was assumed to be constant for each hydrocarbon so that peak area was used as a measure of compound abundance. Areas of individual peaks were normalized to the decane (normal alkane with 10 carbons) peak to compare the relative concentrations of individual compounds in different oil samples. Decane was assumed to have the same abundance in all oil samples. This assumption was based on the fact that all crude oil at the site originally was uniform in composition and that decane has a sufficiently low vapor pressure and solubility not to be volatilized or dissolved.

The percentage of the initial mass (in the original unaltered oil) of each individual compound lost from altered oil samples was calculated by comparing the normalized abundance of compounds in the altered oil to the normalized abundance in the least altered oil from the research site. The least altered oil (from well 604a, fig. 1) was used as a proxy for the original oil because there are no adequately preserved samples of the original oil. The large abundance of volatile compounds in the least altered oil, and the fact that four of the least altered samples have very similar compositions and physical properties, indicate that these samples may closely approximate the composition and physical properties of the original oil. Values of percentage mass loss for individual compounds or the total oil determined are minimum estimates of mass loss, because it was assumed that the least altered oil has the same composition and physical properties as the original oil.

Boiling-point distillations of five crude-oil samples were performed using the Engler method (ASTM D86) to estimate the percentage of the total mass of the oil composed of the lighter-than-dodecane fraction of the oil that was analyzed by GC/MS.

**CHANGES IN OIL COMPOSITION**

The 57 peaks detected in the chromatogram of the oil sample from well 604a are the major peaks and are present in nearly all oil samples (fig. 2). Of the total integrated area under the chromatogram peaks, 74.08 percent was attributable to aliphatic compounds (30.37 percent to normal alkanes, 25.91 percent to cyclic alkanes, and 17.80 percent to branched alkanes), 13.87 percent was attributable to aromatic compounds, and 12.05 percent was attributable to unidentified compounds (table 1). The median carbon number was 7 (C7). Fifty percent of the mass in the analyzed fraction had a carbon number of C6 to C8, 25 percent of the mass had a carbon number of C3 to C5, and 25 percent of the mass had a carbon number of C9 to C11.

Selective loss of aromatic compounds and aliphatic compounds with molecular weights less than nonane has occurred in altered samples of oil from the Bemidji site (fig. 2, table 1). Approximately 50 individual compounds have been depleted in the analyzed fraction. Maximum losses of the total mass of compounds with
Figure 2. Composition of oil samples collected from the Bemidji, Minn., research site in 1989: (A) bar graph representation of a total ion chromatogram of the oil fraction lighter than dodecane for the least altered sample (from well 604a) and (B) percentage depletion of compounds in most altered oil (from well 309). [Peak identifier key: N = Normal alkanes, B = Branched alkanes, C = Cyclic alkanes, A = Aromatics; number following letter indicates number of carbons in molecule (N7=normal alkane with 7 carbons); where more than one compound with the same class and number of carbons is present, compounds are numbered sequentially.]
Table 1. Compounds present and distribution of mass in least altered oil collected from the Bemidji, Minn., research site in 1989 (from well 604a) and minimum, median, and maximum depletions (as percent of initial) of compounds for set of 12 oil samples collected at the site in 1989

[N: Normal alkanes, B: Branched alkanes, C: Cyclic alkanes, A: Aromatics; number following letter indicates number of carbons in molecule (N7=normal alkane with 7 carbons); where more than one compound with the same class and number of carbons is present, compounds are numbered sequentially]

<table>
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<tr>
<th>Compound name</th>
<th>Peak identifier</th>
<th>Retention time, in minutes</th>
<th>Normalized peak area (to decane)</th>
<th>Percentage of area of total resolved peaks</th>
<th>Carbon number</th>
<th>Percentage of compound lost</th>
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the following carbon numbers were measured: C3 (100 percent); C4 (100 percent); C5 (95 percent); C6 (81 percent); C7 (66 percent); C8 (48 percent); C9 (49 percent); and C10 (25 percent). Median losses, by carbon number, for the set of oil samples generally were one-third to two-thirds of the maximum numbers. Because aliphatic constituents have large Henry’s law coefficients, these compounds preferentially partition to the vapor phase from the oil; most aromatic constituents have small Henry’s law coefficients and will preferentially partition into the aqueous phase (Hult and others 1991). Benzene and toluene (C6 and C7 aromatic compounds), will readily partition to both the vapor and aqueous phases from the oil (Hult and others, 1991). Losses of C3-C8 compounds occurred primarily by volatilization of aliphatic compounds. Losses of C9-C10 compounds were primarily by dissolution into ground water and soil moisture of aromatic constituents. Benzene and toluene likely were primarily volatilized; losses by dissolution must have also occurred because losses of benzene and toluene exceeded losses of aliphatic compounds with similar molecular weights and vapor pressures (fig. 2). Methane (C1) and ethane (C2), if initially present in the oil, were not detected in the oil samples and likely were lost from the oil prior to or during the sample collection and storage process because of their high volatility. Because some loss of C3 and C4 compounds may have occurred during sample collection and storage, abundances and losses of these compounds may be underestimated. The total mass of C1-C4 compounds in the original oil likely was relatively small compared to the total mass of the oil; losses of these compounds, therefore, has a negligible affect on the total mass balance of the oil. Maximum percent loss of the total mass in different structural classes of hydrocarbons were normal alkanes (57 percent), branched alkanes (72 percent), cyclic alkanes (62 percent), and aromatics (84 percent). Percent depletions of aromatic compounds, as a class, generally were higher than for aliphatic compounds (table 1). Minimum losses of the total mass of aliphatic compounds, as a class, were 0 percent; minimum losses of the total mass of aromatic compounds, as a class, were 30 percent. These larger depletions of aromatic compounds in otherwise only slightly altered oil samples indicates that dissolution of soluble compounds into water may initially occur at greater rates than volatilization.

CALCULATION OF MASS LOSS

Areal differences in the physical properties of the oil at the site have developed because of variable spatial and temporal alteration rates of the originally uniform oil (Landon and Hult, 1991). Changes in the physical properties of oil during laboratory aging experiments closely matched alteration trends in physical properties measured in the field. The percentage of the initial mass lost from oil collected in the field was calculated using measured changes in the values of physical properties of altered oil samples relative to the least altered oil and relations between percent mass loss and changes in physical properties of oil measured in the laboratory. Linear relations between changes in specific gravity and percent mass loss (fig. 3) and changes in refractive index and percent mass loss exist over the entire range of observed values of physical properties for Bemidji crude oil. The relation between kinematic viscosity and mass loss is nonlinear but systematic. Changes in physical properties of the oil indicate that the rate of mass loss from the original oil ranged from 0 to 1.25 percent per year (average of 0.5 percent per year) and total mass loss ranged from 0 to 11 percent (average is 3.8 percent) since the 1979 spill (Landon and Hult, 1991).

The percentage of total mass lost from altered oil also can be calculated using changes in the composition of the oil. These calculations were performed to compare the values of total mass loss determined on the basis of compositional changes to those calculated using changes in physical properties and to quantitatively determine the compounds and classes of compounds that account for most of the mass loss from the oil. Because the methods of calculating total mass loss based on composition and on physical properties were independent of each other, comparison of results of the two methods is a test of the reliability of the calculations.

Total-mass loss was calculated from changes in oil composition by summing the percentage losses of each individual compound weighted by the abundance of each compound in the least altered oil. Abundance of each compound (as a percentage of the total mass of the oil) was determined from the initial percentage of the mass of the resolved peaks for each compound (table 1) and the percentage of the mass of the oil in the analyzed fraction. Results of the boiling-point distillations indicated that approximately 32 percent of the total mass of the oil had a boiling point less than undecane (normal alkane with 11 carbons), the compound with the highest
Figure 3. (A) Relation of change in specific gravity from initial field value to percent mass loss for oil subjected to volatilization under controlled laboratory aging experiments. (B) Percentage mass loss from oil of original spill composition estimated from changes in composition and specific gravity of oil collected from the Bemidji, Minn., research site in 1989.
Figure 4. (A) Percentage of total oil lost associated with losses of hydrocarbons in each class: minimum, median, and maximum losses for the set of 12 oil samples collected from the Bemidji, Minn., research site in 1989. (B) Percentage of total oil lost associated with losses of hydrocarbons classified by carbon number; minimum, median, and maximum losses for the set of 12 oil samples collected from the Bemidji, Minn., research site in 1989.
that more than 80 percent and 70 percent of the loss of mass from highly altered and median oil samples, respectively, occurs because of volatilization. For slightly altered oil samples (minimum, fig. 4) loss of aromatic compounds accounts for nearly all the loss of mass from the oil.

The largest proportion of the total amount of mass loss is associated with losses of C6 and C7 compounds (fig. 4). Although greater percentage losses of C3, C4, and C5 compounds were due to the greater volatility of these compounds, C6 and C7 compounds were present in greater abundance in the oil than were C3, C4, and C5 compounds, and this greater initial abundance accounts for the greater total loss amount associated with C6 and C7 compounds.

DISCUSSION

Variations in the physical properties and composition of the oil observed in the field have developed from alteration of an originally uniform source. The variations in the composition and physical properties of different oil samples, therefore, represent oil at different stages of evolution from the original oil spilled at the site.

Most of the loss of mass from the oil occurs as a result of volatilization. The effects of biodegradation are poorly known but are likely to be small relative to the effects of volatilization and dissolution. Although percentage losses of aromatic compounds exceed percentage losses of aliphatic compounds, aromatic compounds in the analyzed fraction comprise less than 2 percent of the total oil; losses of aromatic compounds, therefore, are not of major significance in the total mass balance for the oil. The distribution of the aromatics is significant from an environmental perspective because the aromatic compounds make up the vast majority of the contaminant mass dissolved in ground water (Baedecker and others, 1989; Hult and others, 1991).

Essaid and others (1991) found that the oil saturation in aquifer material in the oil bodies at the Bemidji site was highly variable. Even in aquifer material in the middle of the oil bodies no more than 50 percent of the pore space was saturated with oil. The remaining pore space is filled with water and (or) air. There are likely spatial variations in the composition and physical properties of oil on a very fine scale. Such microscale variations may be related to the degree of contact of oil droplets with air and (or) water phases and to the rate at which volatile hydrocarbons in the gas phase or soluble hydrocarbons in the aqueous phase can move away from the oil. These microscale variations in oil properties and composition will not be detected by sampling oil from monitoring wells. The samples collected from monitoring wells represent vertically integrated average samples of the oil in the vicinity of the monitoring well. These bulk average samples, however, are still highly useful for studying the magnitude of the changes in oil characteristics and for calculating bulk or average rates of mass loss from the oil bodies for different areas of the oil pools.

The values of mass loss for the total oil and individual compounds in the oil provide an independent estimate of the spatially variable source term for transport models of volatile and soluble hydrocarbons emanating from the oil source in the subsurface at the Bemidji site. The methods used to quantify these loss rates can be used at other subsurface crude oil spill sites.

REFERENCES


Studies of the Molecular Size of Dissolved Organic Carbon Fractions Downgradient from the Oil Body at Bemidji, Minnesota

By George Aiken

Abstract

Preliminary results of equilibrium dialysis measurements on whole-water samples and isolates of the hydrophobic acid fraction of the dissolved organic carbon (DOC) in ground water at the Bemidji, Minn., toxic-waste study site are presented. Membranes with 2,000 (2K)-dalton and 12,000 (12K)-dalton cutoffs were used. Approximately 10 percent of the DOC in the whole-water sample from well 530 B was excluded from the 2K-dalton-cutoff membrane. Similar results were obtained with aqueous solutions of the hydrophobic acid fraction isolated from water from well 530 B. These results differed markedly from those obtained with aqueous solutions of the hydrophobic organic acid fraction from water from well 310, a background-water-quality well, where approximately 30 percent of the DOC was excluded from the 2K-dalton membrane. Measurements made on whole-water samples from two other wells in the contaminated plume indicate that the amount of organic matter excluded from the 2K-dalton membrane increases with decreasing distance to the oil body, possibly because of organic-matter/iron or organic-matter/organic-matter interactions. The results suggest that colloid-sized organic constituents are generally absent from the ground water but that interactions of DOC with other dissolved constituents could result in an increase in molecular size of DOC fractions.

INTRODUCTION

The U. S. Geological Survey (USGS) study site near Bemidji, Minnesota (fig. 1), is an excellent site for studying interactions controlling organic-compound transport in ground water. In August 1979, a pipeline carrying crude oil burst; the spilled oil contaminated a shallow sand and gravel aquifer. Microbiological degradation of crude oil at the water table has resulted in the development of an extensive plume of dissolved organic carbon (DOC) that has migrated downgradient from the oil body. This DOC is a heterogeneous mixture of organic compounds, most of which are nonvolatile, yellow-colored organic acids that are intermediates in the microbiological degradation of the crude oil (Aiken and Thorn, 1989). In addition, the plume contains distinct redox zones (Baedecker and others, 1989). Measurable concentrations of hydrophobic contaminants, such as phenanthrene, downgradient of the oil body are strong evidence for facilitated transport at this site (Aiken and others, 1992), and the well-defined redox conditions and high carbon content in the mobile and stationary phases make this a desirable site for studying the processes that control solute migration. The interaction of hydrophobic organic species with colloids is a significant, albeit poorly understood, mechanism for transport of hydrophobic organic species in aquatic systems. Although the potential significance of colloids in affecting transport has been recognized (McCarthy and Zachara, 1989; Capel and Eisenreich, 1989), a number of problems associated with the sampling and analysis of colloids have

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hampered research in this area. Preliminary equilibrium dialysis experiments indicate that the molecular sizes of aquatic humic substances from a number of environments are larger than expected on the basis of analyses of molecular weight of organic-matter isolates. Equilibrium dialysis provides information about molecular size rather than molecular weight and has been used successfully to study interactions of hydrophobic organic species with larger humic substances (McCarthy and Jimenez, 1985). In this paper, prelimi-
nary results of equilibrium dialysis measurements for the purpose of estimating the molecular size of organic matter at the Bemidji site are presented. The method used was designed to minimize concentration shifts—an important consideration when studying concentration-dependent phenomena.

SITE DESCRIPTION

The sand and gravel aquifer underlies a pitted and dissected outwash plain; the aquifer is underlain, at a depth of about 20 m, by low-permeability till (Hult, 1987). Aquifer material consists of well-sorted medium quartz sand containing about 6 percent carbonate minerals, 30 percent feldspars, less than 5 percent clay minerals, and less than 2 percent organic carbon (Baedecker and others, 1989). After site-cleanup efforts were completed, approximately 400,000 L of crude oil remained in the aquifer and overlying unsaturated zone. The resulting 2- to 4m-thick lens of crude oil floats on the water table about 8 m below land surface.

In the 14 years since the spill, petroleum, as a separate fluid, has moved about 30 m downgradient, organic constituents in the ground water have moved at least 200 m downgradient, and vapors in the unsaturated zone have moved horizontally about 100 m from the spill. The petroleum source is becoming increasingly viscous, dense, and depleted in volatile organic compounds as a result of selective dissolution and volatilization. Biological degradation of oil components has created an expanding anoxic zone around, immediately under, and downgradient from the spill, and has resulted in the development of distinct redox zones within the plume downgradient from the oil body. Microbiological degradation of crude oil at the water table also has resulted in an extensive plume of DOC that is migrating from the oil body.

METHODS

Samples were pumped from select wells along the plume axis by means of a Keck pump and collected in prebaked, 1-L pesticide bottles. DOC concentrations were determined by use of an Oceanographic International Model 700 carbon analyzer. The hydrophobic-acid isolates were obtained by extraction using XAD resins by the method of Aiken and Thorn (1989). Elemental analyses were performed by the methods reviewed by Huffman and Stuber (1985), and molecular weights were determined by vapor-pressure osmometry by the method of Aiken and Malcolm (1987).

Molecular size-distribution measurements of the DOC in whole-water samples and solutions of isolated organic acids from a contaminated well (530 B) and from an uncontaminated well (310) were made by an equilibrium dialysis technique using Spectrum Spectra/por membranes with 2K- and 12K- dalton molecular weight cutoffs. In addition, molecular size-distribution measurements of the DOC in solutions of potassium acid phthalate and 4-[4-(2-carboxybenzoyl)phenyl]butyric acid also were made. In all cases, the membranes were first soaked in, and then rinsed with, distilled water to minimize the potential for sample contamination by organic materials leached from the membrane. After rinsing, membranes were filled with 50 to 70 mL of distilled water and placed in 1-L widemouth sediment jars containing approximately 950 mL of the solution of interest. DOC concentrations in the solutions both inside and outside the dialysis bags were measured. The ratio of the DOC concentration inside the dialysis bag to the DOC concentration outside the bag (C_i/C_o) was determined for a given solution at a given time to determine the rate and degree of equilibration. All reagents were reagent grade.

RESULTS AND DISCUSSION

The results of equilibrium dialysis measurements on contaminated ground water from well 530 B are given in figure 2. Well 530 B is located in a region of the plume that is a transition zone (Zone 4, according to Baedecker and others, 1989) between the anoxic water near the oil body and the oxygenated, low-DOC waters downgradient. The water in well 530 B had low dissolved oxygen concentrations (≤ 0.3 mg/L, Baedecker and others, 1989), and a DOC concentration of 17.1 mg C/L. After 48 hours equilibration time, C_i/C_o equaled 0.98 in the case of the 12K-dalton membrane and C_i/C_o equaled 0.89 in the case of the 2K-dalton membrane. Neither sample attained equilibrium after 48 hours, as defined by a flattening of the curve.
The results of molecular size-distribution measurements of the DOC in whole-water samples from well 530 B were compared with results obtained using aqueous solutions of standard compounds and isolates of the hydrophobic acid fraction of the DOC in water from well 530 B and in uncontaminated ground water (fig. 3). The elemental compositions and molecular weight data for the isolates and the model compounds are given in table 1. The model compounds were chosen because of the similarity between these compounds and the isolate from well 530 B with respect to polarity and molecular weight. Potassium hydrogen phthalate, which had the lowest molecular weight of the compounds studied, approached equilibrium most rapidly. The hydrophobic acid isolate from well 310 had the highest number average molecular weight (650 daltons) and was the slowest to approach equilibrium. The 530 B hydrophobic acid fraction (335 daltons) and the 4-[4-[(2-carboxybenzoyl)phenyl]butyric acid (CPBA, 313.33 daltons) approached equilibrium at an intermediate rate.

A difference between the standards and the whole-water and isolate samples is that $C_i/C_o$ equaled 1.05 for both of the standards within 72 hours, whereas $C_i/C_o$ was less than 1 for the other samples in the same time (fig. 3). The standards are homogeneous solutions containing a single organic constituent. The DOC in the whole-water sample and the organic matter contained in the hydrophobic acid isolates, on the other hand, is a complex mixture of high- to low- molecular-weight species. The molecular-weight data given for the isolate samples are number-average molecular weights, whereas the data for the standards represent true molecular weights for these species. It is likely that $C_i/C_o$ will not approach 1 if the 2K-dalton membranes for the whole-water and isolate samples are used because of the presence of high- molecular-weight compounds in these samples.
Table 1. Ash-free elemental compositions and molecular-weight data for the hydrophobic-acid fractions isolated from water from wells 530 B and 310, and the corresponding data for phthalic acid and 4-[4- (2-carboxybenzoyl)phenyl]butyric acid.

(Elemental data reported as weight percent)

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<th>Carbon</th>
<th>Hydrogen</th>
<th>Oxygen</th>
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<th>Molecular weight</th>
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<td>650</td>
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</tbody>
</table>

The results of molecular size-distribution measurements of the DOC in whole-water samples from well 530 B were similar to those obtained using aqueous solutions of the hydrophobic acid fraction isolated from well 530 B. After 72 hours, Cj/C0 equaled 0.92 for the hydrophobic acid fraction sample, indicating that approximately 8 percent of this sample was excluded by the membrane (fig. 3). In the original sample, 95 percent of the DOC was accounted for in the solutions inside and outside the membrane, indicating the possibility for sorption of some material on the membrane surface. In addition, complete equilibration across the membrane was not attained with a Cj/C0 of 0.98 using the 12K-dalton membrane (fig. 2). These results indicate the presence of organic components with molecular sizes larger than indicated by the number-average molecular weight of the sample. The difference in results obtained using the 2K-dalton and 12K-dalton membranes also suggests that organic constituents with larger molecular sizes, considered to be material excluded from the 12K-dalton membrane, comprise only a small percentage of the DOC in ground water at well 530 B. It is possible that the large molecular-size material in the water sample from well 530 B is derived from the naturally occurring organic matter in the ground water that contributes to the DOC at well 530 B. A relatively low Cj/C0 of 0.7 was obtained using the 2K-dalton membrane for the fulvic acid sample isolated from well 310 (fig. 3), indicating that approximately 30 percent of the naturally occurring background DOC was excluded (93 percent of the DOC was accounted for in this sample in the solutions inside and outside of the dialysis membrane).

Finally, molecular size measurements of the DOC in whole-water samples from two other wells within the contaminated plume were made using the 2K-dalton membrane. Well 532 B is located in the anoxic part of the plume (Zone 5, Baedecker and others, 1989) -- a zone characterized by the presence of dissolved iron and relatively large DOC concentrations. Well 515 B is located in the oxygenated waters downgradient from well 530 B (Zone 3, Baedecker and others, 1989) that contain little dissolved iron and decreased amounts of DOC. A Cj/C0 ratio was the lowest ratio determined in this study; it increased downgradient to well 515 B where it was 0.9. These data suggest the possibility that either organic matter/iron interactions, or organic-matter/organic matter interactions have produced organic-compound assemblages whose molecular size and weight increase with decreasing distance to the oil body.

REFERENCES


Small-Scale Chemical Heterogeneities in a Crude-Oil-Contaminated Aquifer, Bemidji, Minnesota

By Isabelle M. Cozzarelli¹, Mary Jo Baedecker¹, George Aiken², and Curtis Phinney¹

Abstract

A study of the spatial heterogeneity of biogeochemical reactions was undertaken in an aquifer affected by a crude-oil spill near Bemidji, Minnesota. An anoxic plume extended 90 meters downgradient from the crude-oil body in 1992, and contained elevated concentrations of dissolved organic carbon, methane, ferrous iron, and manganese. Two 1.5-meter-long continuous cores were collected from two locations within the anoxic plume to determine small-scale chemical heterogeneities in the ground water. Chemistry of pore water in a core collected from near the edge of the crude-oil body indicates that oxygenated water does not mix with the anoxic plume. The effects of mixing oxygenated ground water with the anoxic plume is reflected in the chemistry of pore water in a core collected 25 meters farther downgradient; mixing resulted in significant small-scale chemical heterogeneity in the concentrations of organic and inorganic chemical constituents.

INTRODUCTION

The geochemical character of a shallow sand and gravel aquifer near Bemidji, Minn., has been altered by the release of crude oil from a broken pipeline in 1979. Previous investigations at this site documented microbial degradation of monoaromatic hydrocarbons (Eganhouse and others, 1987, 1993; Cozzarelli and others, 1990) and formation of redox zones (Baedecker and others, 1989, 1993; Bennett and others, 1993) downgradient from oil that had accumulated at the water table. The degradation of dissolved organic compounds occurs by aerobic as well as anaerobic microbial degradation processes, resulting in the reduction of manganese and iron and the generation of methane.

Steep chemical gradients have been observed by other investigators in the study of contaminated aquifers (Nicholson and others, 1983; Back and Baedecker, 1989; Cozzarelli and others, 1991; Smith and others, 1991). These gradients can usually be explained by redox boundaries caused by a thermodynamic progression of degradative processes (Baedecker and Back, 1979). Resolution of water-quality problems requires characterization of these chemical heterogeneities in an attempt to understand the factors that control changes in water quality. Novel techniques commonly are required to sample such environments at spatial and temporal scales appropriate to the reactions being studied. This paper describes small-scale chemical heterogeneities in the ground water downgradient from the crude-oil body at the Bemidji research site. The spatial variability of biogeochemical processes and the resulting effects on the fate of degradable hydrocarbons in the plume are discussed.

DESCRIPTION OF THE FIELD SITE

The surficial aquifer is an outwash plain in north-central Minnesota, near Bemidji, (lat. 47°34'25"; long. 95°5'25"). The aquifer was contaminated by crude oil when a pipeline burst in 1979 and sprayed oil onto the land surface (Hult, 1984). Oil reached the water table at a depth of 5 to 7 m below land surface and formed an oil body approximately 1-m thick that floats on the water table (fig. 1). The aquifer sediment is heterogeneous and consists of medium- to poorly sorted, fine- to medium-grained sand near the oil body (D.A. Franzi, State University of New York, written commun., 1989). Estimates of ground-water velocities near the water table range from 0.05 m/d in fine-grained sediment to 0.5 m/d in coarse-grained sediment (Bennett and others, 1993).
Figure 1. The study site at Bemidji, Minn., showing locations of water-table well, cores, the oil body, and oil pipeline. (A-A' is the sampling transect in figure 2.)

STUDY METHODS

Field Procedures

Ground-water samples were collected from water-table wells and deeper wells along a transect in the direction of ground-water flow (fig. 1). Ground-water samples for analysis of unstable constituents were collected with a submersible pump, and ground-water samples for analysis of organic compounds were collected with a Teflon bailer by the methods of Bae-decker and others (1993) and Eganhouse and others (1993).

The 1.5-m-long continuous cores were collected from two locations (A and B, fig. 2) downgradient from the crude-oil body using a modified version of a fixed-piston, wireline-core barrel (Murphy and others, 1996).
The coring method involved drilling with a hollow-stem auger to the top of the desired coring interval, followed by driving of the core barrel beneath the augers to the desired depth. The coring method uses a piston that creates a suction on saturated sediment within the core barrel as the barrel is driven into the sediment. The bottom of the core is frozen *in situ* to prevent loss of fluids out the core bottom. The 47-mm diameter cores were collected in clear polycarbonate liners. The cores were removed from the core barrel and immediately sealed with plugs at the top and bottom after retrieval. The top plug was connected to N₂ gas which was at a pressure of less than 30 kPa during sampling of the core.

Water from the saturated cores was collected at 16-cm intervals beginning at the top of the core. The core was drained at each interval before the next interval was sampled. The pore water was sampled by drilling a 4-mm-diameter hole in the polycarbonate liner and then inserting a leur-tip syringe snugly into the hole. Approximately 10 to 15 mL of pore water was collected at each interval.

Water samples were collected for methane (CH₄) and monoaromatic hydrocarbon analyses without filtration. Samples for dissolved organic carbon (DOC) analysis were filtered through 0.45-μm silver filters. Samples collected for ferrous iron (Fe²⁺) analysis were filtered through 0.1-μm Nuclepore filters. Water samples collected for measurement of CH₄ concentrations were collected in Glasspak syringes. The water sample was transferred from the syringe into 25-mL serum bottles containing enough mercuric chloride (HgCl₂) to produce an Hg concentration of 0.2 mM. Ground water for determination of volatile hydrocarbons was collected in 1.8-mL glass vials containing HgCl₂.

![Diagram](image)

**EXPLANATION**

- Screened interval of sampling sites
- Core
- 0.5 — Line of equal O₂ concentration—
  Interval, in milligrams per liter, is variable

**Figure 2.** Cross section along transect A-A' of the Bemidji, Minn., aquifer showing location of water table and deeper wells, cores, and oil body, and the concentrations of dissolved oxygen for 1992.
### Analytical Procedures

Samples collected for Fe$^{2+}$ analysis were fixed with reagents in the field; Fe$^{2+}$ concentrations were determined colorimetrically by a modified bipyridine method (Baedecker and Cozzarelli, 1992). Dissolved methane concentrations were measured by headspace analysis and gas chromatography (Baedecker and Cozzarelli, 1992). DOC concentrations were measured by the persulfate wet-oxidation technique using a carbon analyzer. Concentrations of volatile monoaromatic hydrocarbons were measured by purge-and-trap capillary gas chromatography using a DB-5 bonded-phase fused-silica capillary column as described by Phinney and Cozzarelli (1996). The hydrocarbons were analyzed by gas chromatography with ion-trap mass-spectrometric detection.

### GROUND-WATER CHEMISTRY AND SPATIAL HETEROGENEITIES

An anoxic zone, approximately 1$\frac{1}{2}$- to 3-m thick, extended 90 m downgradient from the oil body in 1992 (fig. 2). Elevated concentrations of reduced chemical species, CH$_4$ (29.7 mg/L), Fe$^{2+}$ (57.6 mg/L), and Mn$^{2+}$ (2.7 mg/L) were found in this anoxic zone but were at concentrations less than 0.1 mg/L in the background water. The highest concentration of DOC, 35 mg/L, was found in ground water beneath the oil body. The primary processes controlling the oxidation of hydrocarbons in the anoxic zone were identified as microbially mediated iron and manganese reduction and methanogenesis. The steepest gradients in chemical constituents occurred along the edges of the anoxic plume where recharge water and ground water upgradient from the oil body mix with the plume (fig. 2).

At 20 m downgradient from the edge of the crude-oil body, the concentrations of chemical constituents in the pore water from core A indicate that oxygenated water does not infiltrate into the anoxic plume (figs. 3 A,B,C) as illustrated by the high concentrations of DOC, Fe$^{2+}$, and hydrocarbons (total monoaromatic hydrocarbons) that are present less than 10 cm below the water table. Concentrations of Fe$^{2+}$ increased from 2.3 mg/L at the water table to 38 mg/L at about a meter below the water table. The monoaromatic hydrocarbons represent only 4 percent of the DOC within the first meter below the water table. Analyses of pore water in core B from greater than 1 m below the water table, in contrast, indicate that 14 percent of the DOC is composed of monoaromatic hydrocarbons. The remainder of the DOC is most likely composed of nonvolatile compounds, such as hydrophobic and hydrophilic acids that are degradation products of the oil (Eganhouse and others, 1993). The ratios of individual monoaromatic hydrocarbons relative to 1,2,3,4-tetramethylbenzene (1,2,3,4-TMBz) indicate that hydrocarbons that are persistent within the anoxic plume (Eganhouse and others, 1987; Cozzarelli and others, 1990) are degrading by aerobic processes in a thin zone (<1-m thick) near the water table (fig. 3F).

### SUMMARY

The results of this study underscore the need to determine small-scale geochemical changes so that the biogeochemical processes occurring in organic-rich subsurface environments can be evaluated. Pore-water samples from two cores collected downgradient from a subsurface oil body indicate that oxygenated water does not mix with the anoxic plume 20 m from the edge of the oil body. The chemistry of the water at this loca-
Figure 3. Vertical cross sections showing concentrations of:
(A) Methane (CH$_4$) and dissolved organic carbon (DOC);
(B) Total monoaromatic hydrocarbons (HC) and ferrous iron (Fe$^{2+}$); and
(C) Benzene, ethylbenzene, and propylbenzene relative to 1,2,3,4-tetramethylbenzene in pore water from core A as a function of
depth below land surface; and the concentrations of
(D) Methane (CH$_4$) and dissolved organic carbon (DOC);
(E) Total monoaromatic hydrocarbons (HC) and ferrous iron (Fe$^{2+}$); and
(F) Benzene, ethylbenzene, and propylbenzene relative to 1,2,3,4-tetramethylbenzene in pore water from core B as a function of
depth below land surface.

The water table was at 8.9 m below land surface at the location of core A, and at 9.1 m below land surface at the location of core B.
tion is characterized by high Fe$^{2+}$ and CH$_4$ concentrations and DOC, a large fraction of which is composed of monoaromatic hydrocarbons. In contrast, mixing with infiltrating oxygenated water at a site 20 m farther downgradient has produced spatial heterogeneities in the composition of chemical constituents and their concentrations. Aerobic degradation of hydrocarbons in a thin zone near the water table results in their depletion relative to a more conservative organic compound, 1,2,3,4-TMBz. The DOC in this area of the aquifer is composed of mostly nonvolatile hydrocarbons.

REFERENCES


Use of Carbon and Hydrogen Stable Isotopes to Investigate the Production and Fate of Methane at a Toxic Waste Site, Bemidji, Minnesota

By Kinga Revesz\textsuperscript{1}, Tyler Coplen\textsuperscript{1}, Mary J. Baedecker\textsuperscript{1}, and Marc Hult\textsuperscript{2}

Abstract

Stable carbon and hydrogen isotope ratios of dissolved methane and aqueous carbon dioxide in the saturated zone of a crude oil spill near Bemidji, Minn., support the concept of methane production by acetate fermentation with concomitant increase in bicarbonate concentration as opposed to carbon dioxide reduction (and bicarbonate consumption). Oxidation of dissolved methane along the lateral flow path seems to be minimal because no measurable change in isotopic composition of methane occurs with distance from the oil body. As methane from the ground water diffuses upward through a 5- to 7-meter-thick unsaturated zone, it is partially oxidized to carbon dioxide, increasing the $\delta^{13}C$ of the remaining methane, decreasing the $\delta^{13}C$ of the carbon dioxide, and increasing the pressure of carbon dioxide in the unsaturated zone.

No increase of concentrations of atmospheric methane was detected at ground level directly above the oil plume; concentrations were identical to those of a background atmospheric sample.

INTRODUCTION

Although oil spills are becoming increasingly common, few geochemical studies have investigated in detail the production and fate of methane (CH$_4$), one of the products of biodegradation of oil. We investigated CH$_4$ geochemistry at Bemidji, Minn. (fig. 1), where crude oil from a spill floats on the water table in a shallow sand and gravel aquifer. Some components of the crude oil are degraded to CH$_4$ and other products in the ground water by anaerobic microbes. The CH$_4$ produced in the ground water diffuses upward into the unsaturated zone, and is transported horizontally by the ground-water flow. To identify the reactions generating CH$_4$ in the saturated zone at Bemidji, we analyzed CH$_4$, carbon dioxide (CO$_2$), and water for their isotopic compositions.

At Bemidji, substantial amounts of volatile petroleum hydrocarbons are transported from the water table through the unsaturated zone as vapor, which subsequently dissipates to the atmosphere or is biodegraded. An increase in oxygen concentration and a decrease in CO$_2$ concentration toward land surface in the unsaturated zone indicate that volatile hydrocarbons are being oxidized to CO$_2$ (Hult and Grabbe, 1986). Recent gas-chromatographic measurements show that the concentrations of C$_3$–C$_8$ alkanes and CH$_4$ decrease rapidly toward land surface (Hult and others, 1991), although the decrease in CH$_4$ is less than that of the alkanes. Data from Hult and others (1991) indicate that the transport of hydrocarbons in the unsaturated zone is through diffusion coupled with oxidation. To provide information on the sources and sinks of CH$_4$ in the unsaturated zone, we measured the concentration of CH$_4$ and CO$_2$, the hydrogen and carbon isotopic composition of CH$_4$, and the carbon isotopic composition of CO$_2$.\textsuperscript{3}

\textsuperscript{3}We express hydrogen and carbon isotope ratios as delta values given in per mil (parts per thousand, or ‰) relative to a working standard—VPDB (Vienna PeeDee Belemnite) for $\delta^{13}C$ values on a scale normalized such that NBS19 carbonate is +1.95‰ (Hut, 1987) and VSMOW (Vienna Standard Mean Ocean Water) for δD values on a scale normalized such that δD of SLAP (Standard Light Antarctic Precipitation) is -428‰ relative to VSMOW. (Coplen, 1988.)
Figure 1. Bemidji research site, Bemidji, Minnesota: (A) Plan view of site; arrow shows approximate direction of ground-water flow, and (B) hydrogeologic section through the oil plume (modified from Baedecker and Cozzarelli, 1991, fig. 2).
THEORETICAL BACKGROUND

Anoxic aqueous environments are commonly characterized by the formation of biogenic CH₄ (Whiticar, 1986). Two biogenic CH₄ production pathways are commonly recognized: the reduction of CO₂ by hydrogen and the fermentation of acetate. Acetate fermentation refers collectively to methanogenesis that involves the transfer of a methyl group from any substrate. These two pathways can be distinguished on the basis of stable carbon and hydrogen isotope ratios.

The carbon isotope fractionation factor between coexisting CO₂ and CH₄ can be expressed as

$$\alpha_{\text{CO}_2-\text{CH}_4} = \frac{\left(\delta^{13}C/12C\right)_{\text{CO}_2}}{\left(\delta^{13}C/12C\right)_{\text{CH}_4}}$$

(1)

where \(\alpha_{\text{CO}_2-\text{CH}_4}\) is generally 1.05 to 1.09 for reduction of CO₂ and 1.04 to 1.06 for fermentation reactions (Whiticar, 1986). The carbon fractionation factors of the two production pathways overlap. In some cases, carbon isotope data are not sufficient to identify the reaction pathway, as was the case at Bemidji. Therefore, determination of the hydrogen isotope ratios is useful because the isotopic difference between the two CH₄-production pathways is large. The formation water is the only source of the hydrogen in the CH₄ formed by reduction of CO₂. A linear relation between \(\delta D\) in CH₄ and \(\delta D\) in water for the reduction pathway in per mil is (Nakai and others, 1974; Schoell, 1980)

$$\delta D_{\text{CH}_4} = \delta D_{\text{H}_2\text{O}} - 160 \pm 10$$

(2)

For acetate fermentation processes, 25 percent of the hydrogen in the CH₄ is derived from water and the remaining 75 percent is transferred from methyl carbon acetate (Pine and Barker, 1956; Daniels and others, 1980). The relation between \(\delta D_{\text{CH}_4}\) and \(\delta D_{\text{H}_2\text{O}}\) for the reaction in per mil is

$$\delta D_{\text{CH}_4} = 0.25\delta D_{\text{H}_2\text{O}} - 321$$

(3)

Methanogenesis in freshwater usually represents a mixture of acetate fermentation and CO₂ reduction pathways. Many investigators have concluded that fermentation of acetate is the source of about 70 percent of the CH₄ in freshwater (Jenis and McCarty, 1965; Balyaev and others 1975; Cappenberg and Jongejan, 1978; Mountfort and Asher, 1978). The production of CH₄ by CO₂ reduction is thought to be responsible for the remaining 30 percent.

Microbial anaerobic oxidation of CH₄ can also be identified by isotopic abundance measurements, which indicated that the carbon isotope fractionation factor ranges from 1.002 to 1.014, a range that is smaller than that associated with methanogenesis by CO₂ reduction or by acetate fermentation.

EXPERIMENTAL PROCEDURES

A vacuum preparation system and sampling technique were used to determine the \(\delta D\) and \(\delta^{13}C\) values of CH₄. The major experimental steps involved (1) sample collection of CH₄ from ground water, the unsaturated zone, and air, (2) determination of CH₄ and CO₂ concentrations by use of gas chromatography, (3) quantitative separation and conversion of CH₄ into CO₂ and H₂, and (4) isotope-ratio analysis of CO₂ and H₂ by mass spectrometry.

Sample collection of CH₄ from ground water, modified from the method of Oremland and others (1987), involved combining about 50 mL of N₂ with 450 mL of water sample and shaking vigorously for equilibration. The headspace gas mixture was entirely removed by a syringe and it was stored by injecting it into a stoppered, crimped serum bottle (60 mL) that was previously filled with deionized water. The water was partly replaced by inverting the bottle and inserting an 18-gauge needle through the stopper. This procedure allowed recovery of the entire sample without contamination or dilution by air. Furthermore, this segregation of the extracted gases eliminated any possibility of postsampling microbial alteration.

Gas samples from the unsaturated zone were collected from a sampling point 1 m above the center of the oil plume. Samples were collected through 10-cm-long, 6.4-mm-o.d. stainless steel screens attached to 3.2-mm-i.d. stainless steel tubing permanently installed 0.6, 1.5, 2.4, 4, and 5 m below land surface. Sampling tubes were placed in 10-cm-diameter auger holes, and the holes were backfilled with native sand and bentonite (Hult and Grabbe, 1986). Samples were collected in preevacuated 250-mL gas-sample tubes by use of a peristaltic pump by a modified method of Wood and Petraitis (1984). The gas samplers have a stopcock at
each end and an opening with a septum. Aliquots of 10 to 20 mL were extracted for sample preparation by inserting a syringe through the septum.

Air samples 1 m³ in volume were collected from 5 cm above the ground surface directly above the oil plume and about 50 m away from the oil plume (for a background sample). The air samples were pressurized in an aluminum cylinder by use of an oil-free air compressor (Wahlen and others, 1989).

All samples were analyzed for CH₄ concentration and, when necessary, for CO₂ concentration by means of a gas chromatograph with a flame-ionization detector. Gas chromatographic samples were no larger than 1 μL for soil gas samples and 10 mL for air samples to ensure that the isotopic composition of samples was not altered on the basis of mass balance considerations.

Sample preparation for analysis of δ¹³C and δD in CH₄ consisted of (1) separation of the CH₄ from a large volume of air by passing the sample slowly over charcoal at -190°C (Wahlen and others, 1989), which absorbs the CH₄, (2) purification of CH₄ by gas chromatography (Revesz and Coplen, 1990), (3) quantitative oxidation of CH₄ to CO₂ and H₂O by use of a copper furnace at 450°C and a copper oxide furnace at 800°C, and (4) decomposition of water to H₂ by passage over U at 800°C (Bigeleisen and others, 1952). Air samples with a volume fraction of 1 to 3 ppm CH₄ required all four steps. Gas samples with a volume fraction of 5 to 20 percent CH₄ however, did not require preenrichment (step 1) before gas-chromatographic separation. Gas samples consisting of 100 percent CH₄ or containing only inert gases and no other hydrocarbons beside CH₄ were combusted directly. The 1-σ standard deviations of the system if all steps are used are 0.13 % for δ¹³C and 1.55 % for δD values, nearly as small as those obtained for carbonate or water samples by many laboratories.

RESULTS AND DISCUSSION

CH₄ Production in Ground Water

In this study, the concentration of CH₄ and the stable-isotope ratios for CH₄, CO₂, and water were measured along the ground-water flow path. The results are summarized in table 1 and figure 2. Along a flow path at an altitude of around 422 m above sea level, CH₄ concentrations decrease with distance from the oil plume, whereas the δD and δ¹³C ratios for the CH₄ are relatively constant (fig. 2 and table 1). The δ¹³C ratio for dissolved inorganic carbon (DIC) decreases by about 30 % and HCO₃⁻ concentrations decrease between the center of the plume and 100 m downgradient (fig. 2). Baedecker and others (1989, 1993) noted that with time, CH₄ concentrations increased sharply and the δ¹³C of DIC became progressively heavier. The dramatic increase in CH₄ production in 1987 is typically observed in freshwater environments when Fe(III) is no longer available and the δ¹³C of DIC increases (Lovley and others, 1989). Since 1987, there has been no major change in CH₄ concentration or its δ¹³C ratio in the ground water.

In order to identify the pathway for CH₄ genesis, one can look at the relations among δD H₂O, δD CH₄, δ¹³C CH₄, δ¹³C CO₂, and their isotopic fractionation factors (Oremland and others, 1987). As shown in the plot of δ¹³C for CH₄ as a function of δD of CH₄ (fig. 3A), the CH₄ is produced by fermentation. A plot δD of CH₄ and δD for coexisting formation water (modified from Whiticar, 1986) shows that the Bemidji data fall near the line indicating fermentation (fig. 3B). A plot δ¹³C of CH₄ as a function of δ¹³C of CH₄ shows that CH₄ in Bemidji is on the borderline (close to the middle line) between the fermentation and the CO₂ reduction pathways (fig. 3C). From a plot of hydrogen-isotope fractionation factors against the carbon-isotope fractionation factors (fig. 3D), one can see that CH₄ seems to be produced by fermentation at Bemidji. This is the characteristic CH₄ production pathway in freshwater environments and this observation is in good agreement with the study of Cozzarelli and others (1990; 1993 in press), who detected acetate in the ground water at Bemidji.

Furthermore, production of CH₄ by the acetate fermentation pathway is accompanied by production of CO₂, which can react with calcium carbonate to produce bicarbonate. Thus, the high values of bicarbonate that are observed at Bemidji (Baedecker and others, 1989) are inconsistent with acetate fermentation. ¹⁴C studies (Blair and others, 1987) indicate that the methyl group of acetic acid is converted to CH₄. Because the methyl groups of acetic acid are depleted in ¹³C relative to total acetic acid carbon, CH₄ produced by acetate fermentation is significantly depleted in ¹³C relative to acetate. Consequently, inorganic carbon is enriched in ¹³C and its value can exceed 0 % as shown for the Bemidji site in fig. 2.
Table 1. Geochemistry of water samples collected from selected wells, Bemidji, Minn., 1990

<table>
<thead>
<tr>
<th>Well</th>
<th>Distance^ (m)</th>
<th>Altitude (m)</th>
<th>$\delta^{13}$C, CO$_2$ (%)</th>
<th>CH$_4$ Concentration (mg/L)</th>
<th>$\delta^D$ (%)</th>
<th>$\delta^{13}$C (%)</th>
<th>$\delta^{18}$O (%)</th>
<th>Fractionation Factor</th>
<th>$\alpha$ CO$_2$-CH$_4$</th>
<th>$\alpha$ H$_2$O-CH$_4$</th>
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<td>B532B</td>
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<td>421.2</td>
<td>-0.5</td>
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<td>1.20</td>
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<td>--</td>
<td>-84.0</td>
<td>1.15</td>
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</table>

*Estimate of value.

^Dist. is lateral distance to wells and negative values are upgradient.

The decrease in CH$_4$ in the ground water downgradient from the oil plume (fig. 2) can be explained by dilution by native ground water and by the loss of CH$_4$ to the unsaturated zone because $\delta^{13}$C and $\delta^D$ of CH$_4$ change little with distance along the flow path. Had oxidation been an important contributor to the decrease in CH$_4$, the $\delta^{13}$C values of CH$_4$ would have increased along the flow path because oxidized CH$_4$ is depleted in $^{13}$C by as much as 14% (Whiticar, 1986) and the resulting DIC would presumably be depleted in $^{13}$C.

**CH$_4$ Consumption in the Unsaturated Zone**

CH$_4$ concentration and isotopic data for the unsaturated zone are summarized in table 2 and figures 4 and 5. CH$_4$ concentrations are approximately constant within 1 meter of the water table and then decrease gradually to the surface (fig. 4). CO$_2$ concentrations are constant from the water table to within 1 m of the surface. Depth is plotted against $\delta^{13}$C of CH$_4$ and CO$_2$ in figure 5. $\delta^{13}$C values of CH$_4$ are inversely correlated with CH$_4$ concentrations and indicate that the decrease in CH$_4$ concentration toward the surface is caused not only by diffusion but also by a mechanism that preferentially consumes $^{12}$CH$_4$.

One would expect little change in the carbon isotopic composition of CH$_4$ if CH$_4$ concentration decreases solely by diffusion. However, one might expect a change in carbon-isotope composition of
CH₄ Contribution to the Atmosphere

No difference in CH₄ concentration in atmospheric samples was found between a background sample and a sample collected just above the contaminated area; both samples had a CH₄ content of 1.79 ppm by volume. A typical δ¹³C for atmospheric CH₄ is -46‰; -33‰ was measured for the CH₄ gas from the unsaturated zone. The addition of 1 part CH₄ from the unsaturated zone to 1 part atmospheric CH₄ would give an atmospheric concentration of 3.58 ppm by volume and a δ¹³C of -39‰. Thus, these results indicate that carbon-isotope ratios probably cannot be used at Bemidji to quantify transport of CH₄ from the unsaturated zone to the atmosphere.

CONCLUSIONS

A dramatic increase in CH₄ production was observed in the saturated zone above a crude oil plume near Bemidji, Minn. Findings from our study include the following:

In the Saturated Zone:

1. Carbon and hydrogen isotopic ratios of CH₄ support CH₄ production by acetate fermentation (as opposed to CH₄ production by CO₂ reduction).
2. Carbon-isotope fractionation between CH₄ and dissolved inorganic carbon also supports the acetate fermentation production pathway.
3. Oxidation of dissolved CH₄ along the 100-m long flow path investigated seems to be minimal because there is no measurable change in the isotopic composition of CH₄ with distance; therefore, the decreases of CH₄ concentration along the flow path is caused by dilution and the loss of CH₄ to the unsaturated zone.

In summary, the CH₄ production by acetate fermentation in Bemidji is causing an increase in concentration and δ¹³C of dissolved inorganic carbon, apparently because of the intermolecular isotopic inhomogeneity of acetate.
Figure 3. Distinction between acetate fermentation and CO$_2$ reduction methanogenesis by use of isotopes, based on Whiticar’s (1986) data set. (A) $\delta^{13}$C of CH$_4$ as a function of $\delta D$ of CH$_4$. The Bemidji data fall into the area indicating that CH$_4$ is produced by fermentation. (B) $\delta D$ of CH$_4$ as a function of $\delta D$ of formation water. The Bemidji data fall on the fermentation line. (C) $\delta^{13}$C of CO$_2$ as a function of $\delta^{13}$C of CH$_4$. The CH$_4$ production in Bemidji is on the border between fermentation and CO$_2$ production pathways. $\alpha_C$ is the carbon isotope fractionation factor. (D) Hydrogen isotope fractionation factor versus carbon isotope fractionation factor. The CH$_4$ in Bemidji indicates production of CH$_4$ by the acetate fermentation pathway.
Table 2. Geochemical data for the unsaturated zone at Bemidji, Minn., 1991

<table>
<thead>
<tr>
<th>Altitude (m)</th>
<th>Well</th>
<th>CH₄ (vol. %)</th>
<th>CO₂ (vol. %)</th>
<th>δ¹³CCH₄ (%)</th>
<th>δDCH₄ (%)</th>
<th>δ¹³CCO₂ (%)</th>
<th>α CO₂·CH₄</th>
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<tbody>
<tr>
<td>430.5</td>
<td>301.1</td>
<td>0</td>
<td>4.45</td>
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<td>429.5</td>
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<td>1.95</td>
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<td>425.5</td>
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<td>12.26</td>
<td>-42.05</td>
<td>-323.5</td>
<td>-14.95</td>
<td>1.028</td>
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</table>

Figure 4. Change in concentration of CH₄ and CO₂ in the unsaturated zone at Bemidji test site as a function of depth below the surface.

In the Unsaturated Zone:

1. CH₄ is apparently oxidized between 427.5 m and the surface, as indicated by the increase in δ¹³C values and the gradual decrease in CH₄ concentration with decreasing depth.
2. The CO₂ concentration as a function of depth curve is approximately constant below a depth of 1 m, in accordance with oxidation of CH₄ to CO₂.
3. The δ¹³C of CO₂ increases with depth in accordance with oxidation of CH₄ that is depleted in ¹³C. Between the altitude of 425.5 and 427.5 m, the CH₄ and CO₂ is probably a mixture of CH₄ production and consumption. The shapes of the CH₄ and CO₂ distributions in the upper 3 m are consistent with CH₄ consumption (producing a concave upward curve) and CO₂ production (elevated CO₂ concentration at shallow depth).

In the Atmosphere:

No difference in CH₄ concentration in atmospheric samples was found between a background sample and a sample collected just above the contaminated area. Thus, isotope data cannot be used at this test site to quantify discharge of CH₄ from the unsaturated zone to the atmosphere.
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Nakai, M., Yoshida, Y., and Ando, N., 1974, Isotopic studies on oil and natural gas fields in Japan: Chikyyakaya (Geochemistry), v. 7/8, no. 1, p. 87—98.


Sorption of Polycyclic Aromatic Hydrocarbons to Aquifer Materials Containing a Low-Organic Carbon Content from Bemidji, Minnesota

By Joseph J. Piatt¹, Steven J. Eisenriech², Debera A. Backhus³, and Paul D. Capel⁴

Abstract

Three polycyclic aromatic hydrocarbons, naphthalene, phenanthrene, and pyrene — were sorbed to a single sample of aquifer material containing a low-organic carbon content at two different temperatures, 5 °C and 25 °C, using batch and column experimental techniques. Controls on batch and column techniques were incorporated to ensure that the experimental vessels were organic-carbon free, biological and photolytic activity was absent, and solution supernates were colloid-free. The sorptive uptake curves indicated a two-step approach to equilibrium. The data were modelled using a two-site sorption kinetic model. Times to equilibrium were at least 40 hours. Small increases in equilibrium distribution coefficients were observed with decreased temperature which resulted in enthalpy of sorption values which were consistent with a partitioning mechanism. Small decreases in rate constants were occurred as temperature decreased. The values of the solids/water distribution coefficients for the batch experiments were consistently 4 to 60 times larger than those obtained from the column experiments, probably because of differences in experimental boundary conditions or to creation of fine particles in the batch experiments that would increase the surface area available for sorption. Although the relative effects of organic-carbon phase sorption versus mineral phase sorption were not isolated directly, the magnitude of the observed distribution coefficients and rate constants are consistent with sorption controlled by the organic-carbon content of this aquifer material.

INTRODUCTION

Contamination of ground water by toxic organic chemicals has become a national problem (Hult, 1984; Cheremisinoff, 1987). One group of organic chemicals, the polycyclic aromatic hydrocarbons (PAH's), are of particular concern because many are suspected mutagens, teratogens, and carcinogens (Abdul and Gibson, 1986). Thus, the processes that affect the transport and fate of these contaminants in the subsurface must be understood in order to assess exposure risks to humans or other living species and develop efficient and cost-effective remediation strategies.

Sorption is an important process affecting the transport and fate of hydrophobic organic chemicals in aquifer systems. Sorption is a term used to describe the movement of a chemical species between the aqueous and solid phases (Weber 1972; Voice and Weber, 1983). The magnitude of sorption is defined by a distribution coefficient (K_d), which is the ratio of the concentration of species in the sorbed phase to the concentration of species in the aqueous phase. If a chemical sorbs to a stationary sorbent, such as the porous media of an aquifer, its transport will be retarded. If a chemical sorbs to a mobile sorbent phase, such as dissolved organic matter or mobile colloids, its transport will be enhanced as compared to

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Aquifer materials commonly have fractional organic carbon (foc; mass of organic carbon per mass of total dry solids) contents of less than 0.001. There has been little research done on the sorption of PAH's to low foc solids, but it is known that the linear free-energy relations developed for predicting sorption to sorbents with a foc greater than 0.1 do not work as well for low foc sorbents (Schwarzenbach and Westall, 1981; Stauffer and others, 1989; Piwoni and Banerjee, 1989).

Even less well understood are the kinetics of hydrophobic organic chemical sorption to mineral surfaces. Most studies usually allowed 24 to 48 hours for sorptive equilibrium (Piwoni and Banerjee, 1989). Sorptive equilibrium to mineral oxides has been reported to be as short as a few hours (Backhus, 1990; Perlinger and others, 1993). But a recent long-term equilibration study concluded that sorptive equilibrium can take weeks or even years depending on the solute (Ball and Roberts, 1991a). The time-dependent sorption data show an initial rapid uptake followed by a much slower extended uptake of the chemical (Karickhoff, 1980). The presence of organic matter and mineral surface, however, confounds efforts to define a sorptive mechanism. Researchers generally agree that sorption is rate-limited, but they disagree as to the cause. Two major hypotheses exist: the first hypothesis is that rate-limited sorption is due to retarded intraparticle diffusion (Ball and Roberts, 1991b; Harmon and others, 1989). The second hypothesis is that rate-limited sorption is due to intraorganic matter diffusion (Brusseau and others, 1991; Szecsody and Bales, 1989).

Some solute-transport models assume that local equilibrium exists between the solute and the sorbent -- that is, that sorptive interactions are fast compared to advective/dispersive transport (Lapidimus and Amundson, 1952; Gaber and others, 1992). But these equilibrium models do not accurately predict solute movement in transport studies (Brusseau and Rao, 1989; Pignatello, 1989; Harmon, 1989). Some other, more robust, models deal with nonideal transport by incorporating pseudo-first-order rate constants to describe rate-limited physical, transport-related, or chemical-sorption-related processes. Physical processes tend to be rate limited owing to diffusional mass transfer of solutes between mobile and immobile flow regimes (van Genuchten and Wierenga, 1976a, 1976b). On the field-scale, physical nonequilibrium probably dominates nonideal solute transport induced by spatial variations in hydraulic conductivity and distribution coefficients, soil aggregation, and fractures and fissures (Brusseau and Rao, 1989).

Sorption-related nonequilibrium is also important. For hydrophobic organic chemicals, sorption to solids has been shown to be a two-step process: a fast initial solute uptake taking minutes to hours followed by a slower rate of uptake taking days to weeks (Karickhoff, 1984; Ball and Roberts, 1991a). For these chemicals, sorption nonequilibrium is thought to be due to intrasorbent diffusion, and the rate limitations are due to intraorganic-matter diffusion and (or) retarded intraparticle diffusion.

This paper summarizes the results of batch and column sorption experiments, which are used as complimentary techniques to determine equilibrium distribution coefficients and sorptive/desorptive rate constants for experiments conducted at 5 °C and 25 °C. The distribution coefficients obtained from these experiments could be used in ground-water contaminant transport models to predict and interpret the transport and behavior of PAH's in the subsurface.

**MATERIALS AND METHODS**

**Materials**

Naphthalene (greater than 99 percent pure), phenanthrene (greater than 99.5 percent pure) and pyrene (99 percent pure) were chosen as the PAH compounds because of their ubiquity at contamination sites and range of physical-chemical properties (table 1). Sodium bicarbonate (NaHCO$_3$) was used as a background electrolyte.

The sorbent used was an uncontaminated aquifer sample taken from near Bemidji, Minnesota, at a site of a crude-oil spill that occurred in 1979 and that is currently under study by the U.S. Geological Survey as part of its Toxic Substances Hydrology Program (Hult, 1984). The ground water has a pH 7.7 and an alkalinity of about 230 meq/L (Bennett and Siegel, 1987). The bulk aquifer material can be described as a moderately sorted, medium-grained sand containing 57 percent quartz, 30 percent feldspar minerals,
Table 1 - Physical and chemical properties of three polycyclic aromatic hydrocarbons at 25°C and measured sorptive distribution coefficients to aquifer material at 5°C and 25°C

<table>
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<th></th>
<th>Naphthalene</th>
<th>Phenanthrene</th>
<th>Pyrene</th>
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<tbody>
<tr>
<td>Molecular weight (g/mol)</td>
<td>128.2</td>
<td>178.2</td>
<td>202.3</td>
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<td>Vapor Pressure (Pa)</td>
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<td>Molar volume (cm³/mole)</td>
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<td>Water solubility (mg/L)</td>
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<td>.132</td>
</tr>
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<td>Distribution coefficients (mL/g)</td>
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<tr>
<td>batch - 5°C</td>
<td>2.3</td>
<td>3.0</td>
<td>13</td>
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<tr>
<td>batch - 25°C</td>
<td>1.6</td>
<td>2.7</td>
<td>8.3</td>
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<tr>
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<td>column - 25°C</td>
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<td>2.1</td>
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<td>Desorption rate constants (hour⁻¹)</td>
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<td>.030</td>
</tr>
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<td>batch - 25°C</td>
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<td>.067</td>
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<td>.18</td>
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<td>column - 25°C</td>
<td>1.0</td>
<td>.57</td>
<td>.25</td>
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6 percent carbonate minerals, and less than 5 percent clay minerals (Aiken and others, 1991). The bulk material was wet sieved to exclude grain diameters less than 62 μm and greater than 2,000 μm to avoid phase-separation problems in the experiments.

The bulk aquifer material had a fractional organic carbon (foc) of 0.00025 ± 0.00003, the sieved aquifer material had a foc content of 0.00019 ± 0.00008. Sieving the aquifer material had no measurable effect on the foc of the soil. The specific surface area of the soil was measured by a nitrogen three-point surface area analysis. Bulk aquifer material had a specific surface area of 1.37 m²/g. Sieved aquifer material had a specific surface area of 1.08 m²/g. Thus, the portion of the aquifer material removed by sieving accounted for about 20 percent of the bulk soil's total specific surface area.

**Batch Experiments**

Batch experiments were done in 35 mL glass centrifuge tubes. Aqueous PAH solutions were prepared in 0.001 M NaHCO₃ electrolyte solution at greater than 50 percent of their aqueous solubility by adding a small amount of a PAH in methanol stock solution. The amount of methanol added from the stock solutions was always less than 0.05 percent by volume. The same amount of methanol was added to quantitation standards and to control and experimental blanks.

Each experiment consisted of duplicate sets of four tubes. Each set had a control tube that contained only electrolyte solution and the aquifer material. Each set also had three experimental tubes that contained PAH solution and the aquifer material. The amounts of aquifer material and solution were determined gravimetrically through sequential weighing of the tube and cap; tube, cap and soil; and tube, cap, soil, and PAH or electrolyte solution. The mass of sorbent was chosen to ensure that there would be at least a 50 percent difference between initial and final aqueous concentrations at equilibrium. The masses of soil added to the tubes were 20 g, 15 g, and 10 g for naphthalene, phenanthrene, and pyrene, respectively. All centrifuge tubes were filled to the top with solution so that the solutes could not volatilize into a headspace. The tubes were wrapped with aluminum foil to prevent photodegradation.
After filling, the tubes were placed on a wrist shaker and shaken for a predetermined length of time. Times were chosen to maximize the resolution of the sorptive uptake curve. Several "early" time points (0.3, 1, 3, and 9 hours) were chosen in the first few hours of the experiment to coincide with the often reported fast sorption step. After the first several hours, the duration between time points was increased considerably (27, 54, and 100 hours) to accommodate a "slow" sorptive approach to equilibrium.

Following shaking, tubes were centrifuged at approximately 630 to 875 RCF (relative centrifugal force) for about 25 minutes. Part of the supernate was removed via a glass syringe and transferred to 10-mL centrifuge tubes. The tubes were filled to the top and capped with solvent-rinsed aluminum foil-lined caps. These smaller tubes were then centrifuged at approximately 1330 to 1680 RCF for about 45 minutes to remove any traces of fine particles. The supernate from these tubes was analyzed for PAH concentration by fluorescence spectroscopy.

The consistency and constancy of bulk-phase characteristics was monitored throughout the experiments by measuring the pH and specific conductance of the supernate solutions after solute analysis. It was reasoned that if all tubes in a given experiment had consistent pH and specific conductance readings, then all tubes were exposed to the same conditions. In addition, the turbidity of the supernate solutions was measured to detect the presence of colloids.

**Column Experiments**

A column system was designed for continuous flow-through detection. The system consisted of a glass column, stainless-steel plumbing, high-performance liquid-chromatography (HPLC) pumps, glass solution reservoirs, and flow-through fluorescence and specific conductance detectors. The glass column (28 cm in length and 2.54 cm in diameter) was modeled after those used by Lion and others (1990), except it was fabricated from only glass and stainless steel. The ends of the column were slightly rounded to avoid a dead volume. One end of the column formed a cap with a ground-glass base which was mounted on the main column section, which also had a ground-glass base. Stainless-steel frits, 0.5-µm nominal pore size, were seated at the column inlet and outlet. At the column outlet, a small plug of glass wool was placed between the solids and the frit to prevent the frit from becoming clogged with clay-size particles. The column was wet-packed with aquifer material and flushed with 0.001 M NaHCO$_3$ electrolyte solution for approximately 2 days.

HPLC pumps delivered aqueous solutions at 0.8 mL/min, which corresponded to porewater velocities of about 27 cm/hr. This pore-water velocity was chosen because it was as close to estimated actual field pore-water velocities as the pumps could deliver accurately. The general range for other studies is 0.1 to 100 cm/hr. One pump was used to deliver the electrolyte solution and a second pump was used to deliver the PAH solutions. A stainless-steel six-port valve facilitated switching between the two pumps. Three 4-L reservoirs, which were closed to the atmosphere, held the electrolyte, “PAH”, and sodium chloride (NaCl) solutions.

After the column was stabilized with electrolyte solution and the solute solution was equilibrated with the pump parts, a solute front was started to begin formation of the break-through curve (BTC). NaCl was used a tracer to define the hydrodynamic characteristics of the column. Flow rates were checked several times during the course of the experiments to ensure constancy. The column effluent was directed through transfer lines to flow through detectors. NaCl was analyzed using a specific conductance meter and the PAH solutions were analyzed using a fluorescence detector (fig. 1). The influent concentration was monitored at the beginning and end of the solute pulse for constancy. The specific conductance, pH, and turbidity of effluent concentrations were monitored, as they were for the batch experiments.

**RESULTS AND DISCUSSION**

Bulk-solution-phase pH and specific conductance measurements were constant, indicating that sorption and not proton exchange or mineral dissolution was the only process occurring. In the tracer column experiments, transport-related nonideality in the BTC was not observed because the system was homogenous. Thus, sorption nonequilibrium was the only process that caused asymmetric BTC for this system.

Batch and column data sets showed that $K_d$ values increased with a decrease in temperature for a given compound and increased $K_d$ values for more hydrophobic chemicals at a constant temperature. These observations were a direct result of the
increased activity coefficient for the PAH's as the temperature was decreased. The overall increase in $K_d$ values with a 20 °C decrease in temperature, however, was only about 1.4 to 1.6 times. Independent analysis of the contributions of organic-carbon and mineral phases to total sorption indicated that organic carbon was the major contributor to total sorption, even though the Bemidji aquifer material had a low fraction of organic carbon (0.00019). In addition, the thermodynamic data, calculated from the observations at two temperatures, indicated small enthalpy of sorption values (van der Waal's forces) consistent with partitioning of the PAH's into the aquifer material's organic carbon. Entropy values greater than measured in these experiments might suggest the formation of hydrogen-bonds indicating mineral-phase contributions to sorption due to solute/sorbent specific interactions. The batch $K_d$ values were consistently larger than the column $K_d$ values, either because (1) modeling the column data entails normalizing the aqueous solute concentration to the total volume of the system, whereas calculation of batch-derived $K_d$ values normalizes the aqueous concentration to the volume of solution only, or (2) the residence time of the PAH's in the column experiments did not allow true sorptive equilibrium to be obtained.

Figure 1. Breakthrough curves for duplicate experiments of naphthalene, phenanthrene, and pyrene at 5 °C for the column studies. Duplicate experimental runs for the same compound produced identical breakthrough curves. The relative aqueous concentration is the measured concentration divided by the influent concentration. The lines are mathematically modeled break-through curves.
The kinetic data from the batch studies showed a characteristic two-step approach to equilibrium: initial fast decrease in solution concentration occurring over 30 minutes to 2 hours, followed by a slow, extended decrease in aqueous concentration (fig. 2). Sorptive equilibrium was attained after about 40 hours for naphthalene and phenanthrene and longer than 100 hours for pyrene. The data was mathematically described using the two-site sorption kinetic model, which is based on the assumption that a fraction of the total sorptive sites will be rate-limited.

The desorption-rate constants decreased by a factor of 1.5 to 2.5 as the temperature decreased for batch and column experiments, except for the batch experiments with naphthalene (table 1). At a given temperature, the rate constants decreased as the hydrophobicity of the chemical increased. The retarded intraparticle-diffusion model predicted the magnitude
of this effect because of increased $K_d$ values and decreased aqueous diffusion. The intraorganic-matter diffusion model also predicted a decrease in desorption rate constants with a decrease in temperature as the result of a decrease in the polymer diffusion coefficients.

**SUMMARY**

Although the relative effects of organic-carbon sorption compared to mineral-phase sorption were not directly separated, it appears that the organic-carbon content, although very small, controls the rate and extent of sorption because the bonding forces are weak, the rate constants were much smaller than those reported for site-specific sorption, and the organic-carbon phase was responsible for most of the sorption.

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Investigations of Microbial Weathering of Minerals

By Philip C. Bennett and Franz K. Hiebert

Abstract

Mineral weathering in an oil-contaminated aquifer near Bemidji, Minnesota, was investigated using *in situ* methods. Small microcosms containing clean, freshly fractured, mineral fragments were suspended for ~1 year in wells penetrating the aquifer, and the mineral surfaces were then examined for evidence of microbial colonization and mineral diagenesis. After reaction, feldspar and quartz surfaces were lightly colonized with a variety of microfauna. Feldspars were deeply etched in the vicinity of attached microbes, whereas an unidentified clay precipitate was found on uncolonized surfaces of the same fragment. Quartz was lightly etched, with a generally roughened surface and scattered triangular etch pits, whereas most of the calcite showed evidence of carbonate precipitation. These results, combined with 10 years of geochemical data collected at the site, illustrate a complex geochemical system where microbial processes drive multiple reactions that are reflected in the mineral-surface diagenetic textures.

INTRODUCTION

In 1979, a petroleum pipeline rupture near Bemidji, Minnesota, contaminated an unconfined sand and gravel aquifer (Hult, 1984). The hydrology and geochemistry of the site has been intensively studied for the past decade (Baedecker and others, 1993; Bennett and others, 1993; Eganhouse and others, 1993). Although a wide variety of hydrologic and geochemical processes has been documented, a recurrent finding is that microbes affect oil fate, ground-water geochemistry, and mineral diagenesis. Reported here is direct evidence for mineral weathering associated with the presence of oil degrading native microbes.

Study Area Physiography and Hydrogeology

The study site is a shallow sand and gravel aquifer near the small city of Bemidji, in the Bagley outwash plain (fig. 1). The aquifer material is typical for the region, consisting of outwash and morainal sands and gravels, with interbedded lacustrine silts (Franzi, 1988). The ground water in this heterogeneous and largely permeable aquifer flows generally northeastward through the site at a rate of 0.05 to 1.0 m/d (White, 1991). Hydraulic conductivity ranges from 0.02 to 5 cm/s. The lacustrine silt deposits near the water table have the lowest conductivities. Locally, the aquifer is recharged by surface infiltration and discharges to a small lake northeast of the site (Bilir, 1992).

Ground-Water Geochemistry

Details of the inorganic ground-water chemistry have been summarized in Bennett and others (1993) and Baedecker and others (1993). Background water is a dilute Ca-Mg-HCO3 type, with minor concentrations of silica and trace concentrations of Na, K, and Sr. In the contaminated area, the water gains Ca, Mg, dissolved inorganic and organic carbon (DIC and DOC), silica, and iron by the aerobic and anaerobic degradation of oil followed by reaction with silicate and carbonate minerals. Downgradient oxygen is reintroduced, aerobic oil oxidation continues, and the water gradually returns to nearly background conditions (Baedecker and others, 1993).
Changes in chemical characteristics along the contaminated ground-water flow path suggest that several fundamental diagenetic reactions occur. In areas of aerobic degradation, increasing Ca, Mg, and DIC concentrations suggest that carbonates are dissolving, whereas increasing Fe$^{2+}$ concentrations in anaerobic areas suggest that iron minerals are undergoing reductive dissolution (Baedecker and others, 1993) coupled with carbonate precipitation to buffer pH (Bennett and others, 1993). An increase in dissolved silica (from 20 to >60 mg/L) under the oil suggests that silicate minerals also are dissolving. Indirect evidence of quartz and feldspar dissolution was obtained by SEM examination of native aquifer sands (Bennett and Siegel, 1987), but these studies assumed that the precontamination grain surfaces were pristine and not previously altered by other geochemical processes. The goal of the study reported here is to characterize mineral-water reactions by examining surface alteration of pristine mineral fragments.

**METHODOLOGY**

Our *in-situ* microcosms consist of clean mineral fragments within a specified ground-water flow path in order to characterize macroscopic and microscopic surface alteration during a known reaction period. We are examining a range of mineral types, including quartz, microcline, albite, anorthoclase, calcite, dolomite, biotite, and muscovite. Mineral specimens were crushed to a size range of 5 to 20 mm, and the selected fragments were cleaned by brief sonication in distilled water and were air-dried. Multiple 20 g monomineralic and mixed-mineral splits were prepared for use in field reaction, field background, and laboratory control experiments, as well as for permanent archive. In the most recent experiment, each mineral fragment was also scribed with a unique identification code, and weighed to the nearest 10 μg, and the total surface area and microporosity of a complete microcosm fragment population were determined by standard krypton and argon-sorption methods, respectively.

After preparation and characterization, mineral fragments were placed in porous 15 mL polyethylene containers, and four to eight filled containers were assembled in a polyethylene mesh and sterilized. The sterile microcosms were suspended in the screened part of the aquifer by nylon monofilament, and the well bore was purged with nitrogen and sealed for a period of 10 to 14 months (fig. 2). Laboratory control experiments were divided into an archival fraction and a fraction that was immersed in distilled water. After recovery the microcosms were preserved in 2 percent glutaraldehyde at 2 °C until analysis; similar procedures using reserved control experiments did not result in detectable surface-texture artifacts.

In the laboratory, selected fragments were prepared for scanning electron microscope examination by dehydration and critical-point drying before stub-mounting and gold-coating. The attached microbial population was examined for density.
attachment, and morphology, and the mineral surface was examined for evidence of biogeochemical precipitation and dissolution. A subset of mineral fragments was sonicated to remove adhering material and was similarly examined for weathering features. The geochemistry of the silicate surfaces was examined by SEM with energy dispersive analysis of X-rays and by sequential leaching techniques (Berndt, 1987). In particular, organic carbon coatings, carbonates, and iron precipitates were examined. The current experimental series will also characterize mass loss and gain caused by dissolution and precipitation reactions, and changes in microporosity.

RESULTS TO DATE

Three years of data have been collected from a total of 24 field-reaction microcosms. Mineral surfaces were characterized for microbial colonization, microfauna morphology and attachment, surface chemistry, and diagenetic textures. Preliminary leaching experiments have also been completed to characterize the chemistry of the surface precipitates. The results to date for three mineral groups are summarized here.

Quartz

The quartz fragments from the control experiments consist of clean fractured surfaces with fine ridges and steps (fig. 3a). No evidence of chemical weathering or remnant inclusions is visible. After reaction in the contaminated aquifer, many of the surfaces had been colonized by a variety of bacteria seen as individual organisms rather than as biofilms. Much of the visible quartz surface is subtly roughened by extremely fine pitting or more extensively etched in some areas to produce distinctive triangular etch pits (fig. 3b).

Feldspars

The control feldspar surfaces are clean and unweathered, with evidence of linear steps along cleavage and very small ellipsoidal inclusion pits (fig. 4a). As with quartz, some of the reacted feldspar surfaces were colonized, while other surfaces remained uncolonized. The colonized surfaces show evidence of intense chemical weathering, with deep prismatic etch pits oriented along inferred cleavage planes (fig. 4b). The pits are several microns wide.
and over 1 μm deep, with irregular edges. Little evidence of clay mineral precipitation is seen around the etched areas except for thin strands of an unknown amorphous material (fig. 4b). Uncolonized surfaces on the same grain, however, are unetched, and support extensive aluminous clay precipitates (fig. 4c).

Calcite.

Calcite fragments used in the microcosm experiments were prepared in a manner similar to the silicates, except that the duration of the water rinses was much shorter. The clean rhombohedral crystal fragments exhibit flat surfaces with regular 100 to

Figure 3. Scanning electron microscope micrographs of quartz fragments. (a) Clean quartz fragment from control group; (b) etched quartz fragment from the field reaction group, showing roughened surface and triangular etch pits.

Figure 4. Scanning electron microscope micrographs of microcline fragments. (a) Clean microcline surface from control group showing cleavage and remnant inclusion features; (b) etched feldspar surface from field-reaction group; (c) unetchd surface from field-reaction group showing precipitated kaolins.
500 nm high steps where cleavage planes have been fractured during crushing (fig. 5a). After reaction for ~1 year, only very sparse microbial colonization was found, and the amount of colonization was much less than that on the silicate surfaces. Where bacterial colonization was observed, etching of the mineral surface was evident, and was characterized by deep irregular prismatic dissolution pits along cleavage planes (fig. 5b).

The most common surface alteration of calcite was precipitation of calcite overgrowths. Growth of 500-nm-thick tabular calcite on the previously clean surfaces was recorded on almost all crystal faces examined. A hypothesized crystal-growth progression begins with 100- to 500-nm-high individual spikes extending upward from a flat background surface (fig. 5c). The spikes form straight rows and rhombohedral enclosures uniformly 1000 nm across. The open enclosures of calcite spikes fill to form isolated plateaus 500 nm high that apparently coalesce into sheets of smooth calcite, thus adding a new layer to the original calcite grain (fig. 5c).

**DISCUSSION**

Previous research into silicate and carbonate weathering at the Bemidji site relied on geochemical characterization of ground water and examination of native sand grains collected from contaminated and pristine locations (Bennett and others, 1993; Baedecker and others, 1993; Bennett and Siegel, 1987). This approach suggested that silicates are weathering, but the rate and extent of dissolution of a specific silicate type is obscured by lack of knowledge of the starting condition of the mineral surface. Similarly, the carbon mass-balance calculations suggest that a carbonate mineral may be precipitating in the anoxic region under the oil (see, for example, Baedecker and others, 1993), but the composition of the mineral and the rate of precipitation were unclear. In both cases, the role of microbes was unknown and initially was thought to be primarily as net producers of carbonic and organic acids released directly into the bulk ground water.

The experimental results described here suggest that microbes in this aquifer colonize fresh mineral surfaces, resulting in a non-uniform pattern of attached biologic material. In the vicinity of attached microbes, feldspar and quartz dissolve, even in waters greatly supersaturated with respect to quartz. We hypothesize that attached microbes on the surface create a microreaction zone, where extremely high...
concentrations of extracellular organic ligands accumulate (Hiebert and Bennett, 1992). In this small area, silicate weathering is greatly enhanced, increasing both the dissolution rate due to ligand-promoted mechanisms and the solubility due to solution complexes. The rate of feldspar dissolution, inferred from an estimate of mineral volume removed, is many times faster than that predicted from inorganic experimental systems (Bennett and others, 1991; Hiebert and Bennett, 1992).

Uncolonized silicate surfaces, in contrast, are unweathered or show evidence of clay precipitation. Away from the microbial microreaction zone, the reactive ligands and chelated products of dissolution mix with the bulk aquifer water, possibly shifting equilibria from that established at the dissolving surface. This water may be greatly supersaturated with respect to kaolin-group minerals, thus precipitating aluminum as a kaolinite or halloysite and leaving excess silica in solution. This hypothesis is supported by the chemical composition of the ground water, where silica concentration increases greatly, but aluminum concentration never exceeds 2 μM (Bennett and others, 1993). We are currently investigating the possibility that microbes preferentially colonize the upstream side of a fragment, where microfauna will first attach and where nutrients are supplied by flowing ground water.

In the carbonate system, the microbial use of iron oxide as an electron acceptor for carbon metabolism may shift the carbonate geochemistry toward calcite supersaturation by increasing pH and producing bicarbonate (Bennett and others, 1993). Calcite precipitates, forming the distinctive overgrowth morphologies seen on the cleaved calcite fragments. The form of the carbonate precipitate and results of EDAX analysis of the individual spikes suggest that the calcite is nearly pure, with no detectable iron or magnesium. We are presently investigating the controls on the geometry of calcite overgrowth spikes, and overgrowth step height.

CONCLUSIONS

This ongoing study of microbial processes in an oil-contaminated aquifer suggests that native microfauna have a significant effect on mineral-weathering mechanisms and rate. Where microbes attach to silicate surfaces, microenvironments produced by metabolic processes greatly enhance silicate dissolution. The rate and extent of dissolution cannot be evaluated from the bulk chemical composition of the water, because this is a dilute reflection of the environment immediately adjacent to a metabolizing microbe. The nature of this microenvironment and the types and concentrations of reactive ligands are expected to be affected by the biogeochemical environment, the nature of the carbon substrate, and the availability of nutrients. In the nutrient-poor, anoxic, and carbon-rich environment of the Bemidji aquifer, the microbial microenvironment apparently is very aggressive toward silicate minerals. The carbonate system, in contrast, is apparently perturbed by the overall biogeochemical reactions that consume the carbon in petroleum, resulting in calcite precipitation.

The in situ microcosm approach allows for the direct examination of the form and rate of both silicate dissolution and calcite precipitation in low-temperature systems using well-characterized starting surfaces. By combining surface-texture examination with long-term geochemical characterization, rock-water reactions can be demonstrated directly.

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Multiphase-Flow Modeling of the Bemidji, Minnesota Crude-Oil-Spill Site with Geostatistical Simulation of Hydraulic Properties

By L.A. Dillard1,2, H.I. Essaid2, and W.N. Herkelrath2

Abstract

This paper describes a study aimed at improving the understanding of multiphase flow in a heterogeneous aquifer by using data collected at the north pool sub-region of a crude-oil-spill site near Bemidji, Minnesota. Data collected include grain-size distributions, oil and water saturations, and porosities of samples collected at the north pool site. These data are used to estimate permeability (k), retention curves, and the geometric mean and standard deviation of the sampled grain-size distributions. The k estimates are statistically distributed in a bimodal log-normal fashion, whereby the two k population distributions correspond to the two predominant aquifer lithologies at the north pool: a coarse glacial-outwash deposit and interbedded fine-silt lenses. A dual geostatistical approach involving sequential indicator and Gaussian simulation is used to characterize the bimodal aquifer heterogeneity present at the north pool by creating one realization of a three-dimensional grid of log(k) values conditioned on the original data.

Field oil-saturation data indicate that the spatial distribution of oil in the subsurface has been affected by the bimodal aquifer heterogeneity present at the north pool. The shape of the subsurface oil-saturation distribution is highly irregular; more specifically, the center of the oil lens is actually depressed below the water table in some locations, and oil saturations almost as high as 0.3 occur in the unsaturated zone. A cross-sectional numerical model is used to simulate the flow of oil and water at the north pool, assuming the air phase is at atmospheric pressure. A slice of the three-dimensional grid of log(k) values produced through geostatistical simulation is used as input in the multiphase model to investigate the effect of aquifer heterogeneity on multiphase flow. Flow simulations using the bimodal representation of heterogeneity produce an oil-saturation distribution that is similar to that found in the field. Other factors affecting multiphase flow, such as hysteresis and three-phase oil relative permeability, also are investigated. The effects of hysteresis are not as significant when heterogeneity is adequately characterized.

INTRODUCTION

Contamination of ground water by nonaqueous-phase liquids (NAPL's) is a problem that has become increasingly prevalent in hydrogeology. Such NAPL's can range from synthetic organic compounds such as trichloroethylene (TCE), to natural and refined hydrocarbons such as crude oil. A limited amount of work has focused on the effects of spatial variability on the movement of NAPL's in the subsurface. Previous work includes one- and two-dimensional laboratory experiments on the distribution and movement of oil (Schwille, 1984, 1988; Schiegg and McBride, 1987; Kueper and others, 1989), and numerical simulations.
of two-phase flow (Kueper and Frind, 1991a, b). Laboratory experiments are unrealistic representations of field-scale processes. Furthermore, because NAPL contamination problems often involve infiltration of NAPL and water into the unsaturated zone, numerical simulations should include the three-phase flow of air, water, and NAPL. Petroleum engineers have shown that reservoir spatial variability can have a significant effect on multiphase flow (Haldorsen and Chang, 1986; Lasseter and others, 1986). However, because hydrogeologists work at a more shallow and local scale, small-scale heterogeneities that can be overlooked at the reservoir scale need to be incorporated into the hydrogeologist's model.

The extensive fluid saturation and sediment data set acquired at the Bemidji crude-oil-spill site prompted an investigation of the effect of aquifer heterogeneity on three-phase flow in the field. A portion of these data was used in previous studies of the effect of heterogeneity on multiphase flow (Essaid and others, 1993; Essaid and Hess, 1993; Essaid and others, 1991). However, these previous studies used data from the south pool sub-region of the Bemidji field site where the aquifer does not display the complex bimodal heterogeneity present at the location of the present study, the north pool. Consequently, the geostatistical simulation techniques used in the previous south pool studies to characterize aquifer heterogeneity do not apply to the more complex heterogeneity analyzed in the present north pool study.

The purpose of the north pool study is to explore and challenge the results of the previous south pool study. The current north pool study offers a more detailed examination of the effects of aquifer heterogeneity on multiphase flow, and it explores the significance of other factors affecting the migration of oil, water, and air in the subsurface. This paper briefly describes the contamination history of the entire Bemidji site and the north pool data used in the current study. A numerical aquifer that represents the bimodal heterogeneity present at the north pool is generated using geostatistical simulation. This numerical aquifer is used in multiphase flow simulations to ascertain the effect of heterogeneity on the flow of water and oil in the presence of air in the subsurface. Other factors affecting multiphase flow in a heterogeneous aquifer, such as hysteresis and three-phase oil relative permeability, are also investigated.

**SITE DESCRIPTION**

In August 1979, a submerged pipeline ruptured and spilled crude oil at a site near Bemidji, Minnesota. The topography of the Bemidji site consists of mostly flat terrain with gently undulating hills; most of the area is underlain by a coarse glacial outwash deposited during the most recent glaciation. Because the crude oil was under pressure when it spilled, much of the oil was sprayed over the area. The crude oil eventually settled, either by flowing from the point of rupture or by being sprayed, in two topographic depressions, termed the north and south pools. Despite the proximity of the north and south pools at the site, the local geology at each is quite different. The south pool is underlain almost exclusively by coarse glacial outwash, whereas the north pool is underlain by glacial outwash with interbedded silt lenses (Franzi, 1988). Previous studies focused on data from the south pool; the focus of the present study is on the more heterogeneous north pool.

Since the time of the pipeline rupture, numerous boreholes have been drilled at the entire site. For the purpose of this study, data from 613 core samples collected from the north pool are analyzed. The cores were obtained from 20 boreholes aligned along a 90-m-long transect approximately parallel to the direction of groundwater flow (fig. 1). Some (269) of the core samples were collected by the authors and are 7.8 cm in length. The remainder (344) of the core samples were collected by Dave Franzi and are variable in length (Dave Franzi, State University of New York, Plattsburg, written commun., 1989-93). Grain-size distributions were determined for all 613 core samples, and oil and water saturations and porosities were determined for the subset of 269 core samples using the methods of Hess and others (1992). Following the procedure of Krumbein and Monk (1942), permeabilities were estimated for all 613 core samples on the basis of the grain-size distribution data. Soil moisture retention characteristics were estimated for the subset of core samples by the method of Arya and Paris (1981), and retention curves were fitted to the estimated points by means of a van Genuchten function (van Genuchten, 1980).

Fluid saturation and grain-size distribution data suggest that the north pool aquifer heterogeneity has a significant effect on the flow of crude oil, water and air at the site. Measured oil saturations in the unsaturated
zone are as high as 0.3 (fig. 2). Silt lenses in the unsaturated zone appear to have impeded oil infiltration and trapped this oil. Silt lenses at the water table also appear to have an effect on the spatial distribution of the floating oil and lateral oil migration. Profiles of the following sampled data from borehole 016 illustrate the effect the fine fraction of sediment has on multiphase flow (fig. 3): percent grain size less than 1 mm, oil saturation, and water and total fluid saturation. Note that in borehole 016 the peak oil saturation is below the water table. Apparently, the oil follows a high permeability pathway that is located beneath a silt lens.

GEOSTATISTICAL MODELING of AQUIFER HETEROGENEITY

Summary Statistics

The statistical distributions of permeability (k), van Genuchten retention curve parameters (α and n), geometric mean (gmean) and standard deviation of the grain-size distribution (gstd), and porosity, are analyzed using probability plots and histograms. Permeability is the most useful parameter for characterizing aquifer heterogeneity, because it is distributed in a lognormal bimodal fashion with the two
Figure 2. Hydrogeologic section of subsurface showing oil saturation distribution as determined through sampling at the north pool site. Line of section shown in figure 1.
population distributions corresponding to the coarse glacial outwash and the fine-silt lenses. A cut-off of \( \log(k) = -11.957 \) \([\log(m^2)]\) is used to separate the coarse and fine population distributions.

**Variogram Analysis**

The variogram can be used as a tool by which the degree of spatial continuity of a random function can be quantified. The following variograms are calculated and modeled in the vertical and horizontal directions: variograms that use an indicator transform of \( \log(k) \) to estimate the probability that \( \log(k) \) will be less than or equal to the specified cut-off (indicator variograms); and variograms of coarse \( \log(k) \) that have been transformed to fit a normal distribution (normal scores variograms). The indicator variograms provide a measure of the spatial correlation of the indicator transform of \( \log(k) \) for the specified cut-off (Johnson and Dreiss, 1989). In other words, the indicator variogram provides a measure of the connectivity of the highs and lows, that is, the coarse glacial outwash and the fine silt lenses, respectively. On the other hand, the variograms of the normal scores transform of coarse \( \log(k) \) provide a measure of variability within the coarse glacial outwash. Variograms are modeled by visually fitting a combination of nested exponential and spherical structures. Such a combination of nested models is needed to capture the rapid increase in variance at low separation distances or lags, and to represent the relatively slower increase in variance to the sill at larger lags. A summary of the correlation structure of each variogram is in table 1. The models for the indicator and normal scores variograms are used in sequential stochastic simulation.

**Sequential Stochastic Simulation**

Kriging is a linear estimation procedure through which values of a random variable at unsampled points are calculated, given measured values of the random variable at sampled points. When kriging is combined with a multi-Gaussian or nonparametric (indicator) estimation approach, it not only provides a linear estimator, but it also identifies the posterior conditional cumulative distribution function (ccdf) (Deutsch, 1992). The posterior ccdf is an integral part of the sequential simulation process. Furthermore, if a different random path of estimation is taken in each sequential simulation, a series of equally-probable yet different results can be achieved. The uncertainty that can be quantified upon accumulation of such results characterizes stochastic simulation. Two such
Table 1. Correlation structure used to model indicator variograms of log(k) and variograms of normal scores transform (NSC) of coarse fraction of log(k)

[Note: $\gamma$ denotes the semivariogram, exp denotes an exponential model, and Sph denotes a spherical model]

<table>
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<tr>
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<th>Indicator of log(k)</th>
<th>NSC coarse fraction of log(k)</th>
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<tr>
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<td>vertical</td>
<td>$\gamma(h) = 0.04 + 0.04\exp(2h) + 0.01735\text{Sph}\bigg(\frac{h}{8}\bigg)$</td>
<td>$\gamma(h) = 0.229 + 0.687\exp(h) + 0.084\text{Sph}\bigg(\frac{h}{8}\bigg)$</td>
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<tr>
<td>horizontal</td>
<td>$\gamma(h) = 0.04 + 0.04\exp\bigg(\frac{h}{20}\bigg) + 0.01735\text{Sph}\bigg(\frac{h}{80}\bigg)$</td>
<td>$\gamma(h) = 0.229 + 0.687\exp\bigg(\frac{h}{40}\bigg) + 0.084\text{Sph}\bigg(\frac{h}{80}\bigg)$</td>
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Geostatistical estimation procedures are sequential Gaussian simulation (GSS) and sequential indicator simulation (ISS). The correlation structure described by the indicator and normal scores variograms are used in ISS and GSS respectively to construct a permeability distribution conditioned on the original data. Only one realization is generated because the intent of the geostatistical estimation procedure is to produce not a host of equally probable results, but one realization that demonstrates detailed aquifer heterogeneity and can be used in flow simulations.

In geostatistical estimation procedures, if the phenomenon under study is a mixture of different physical or statistical populations, the geometry of the mixture should be modeled and simulated first; then the attribute within each population can be simulated (Deutsch and Journel, 1992; Journel and Isaaks, 1984). The bimodal north pool aquifer heterogeneity is reproduced by using a dual estimation approach to generate a three-dimensional grid of log(k) values conditioned on the original data. ISS is used to describe the structure of the two log(k) classes representing the fine silt and coarse sand population distributions. GSS is used on the normal scores transform of the coarse fraction of the original data to reproduce the spatial variability within the coarse outwash deposit. The GSS approach is not used on the fine population distribution due to the limited amount of conditioning data available representing fine material. The final distribution is obtained by substituting GSS values for ISS values at each node where the ISS value is greater than the specified log(k) cut-off, indicating the presence of coarse-grained sand deposits. This combined k distribution (IGSIM) not only shows the structure of the fine silt and coarse sand deposits, but also the variability within the coarse sand.

A vertical slice of the three-dimensional simulation result is then taken along an extended 180-m-long transect at which the original boreholes are located. Examples of one realization each of GSS and IGSIM can be found in figures 4b and 4c. These slices of GSS and IGSIM of log(k) values are used as input into the cross-sectional numerical multiphase flow model.
A. Uniform mean
\[ \log(k) = -11.28 \, [\log(m^2)] \]

B. 
\[ \log(k) \, [\log(m^2)] \, 433.0 \]

C. 
\[ \log(k) \, [\log(m^2)] \, 433.0 \]

Figure 4. Sections showing permeability distributions (left) and resulting simulated oil saturation distributions (right) for conditions of (A) uniform mean permeability field, (B) coarse permeability field generated using sequential Gaussian simulation (GSS), and (C) bimodal permeability field generated using joint sequential indicator and Gaussian simulation (IGSIM). Datum is sea level and origin for horizontal distance is borehole 707 as shown in figure 1.
NUMERICAL MULTIPHASE-FLOW MODELING

The objectives of the numerical modeling are threefold. The first goal is to investigate the appropriateness of the assumptions used in the model. The second objective is to produce a simulated oil saturation spatial distribution similar to the observed oil saturation distribution. For this purpose, the oil saturation data are used not as a matching device but as a clue to the subsurface spatial structure of the oil body. Of course, given the amount of uncertainty in model parameters and approximations, the simulated oil saturation distribution will never exactly match the observed oil saturation data. Therefore, the third goal of the study is to conduct a sensitivity analysis of the factors most affecting multiphase flow and the resulting oil saturation distribution.

A vertical, two-dimensional, numerical model that simulates the flow of oil and water is used (Essaid and others, 1993). The model is based on the assumption of atmospheric air pressure and includes spatial variability of soil hydraulic properties using Miller and Miller scaling (Miller and Miller, 1956) and hysteresis with oil entrapment. The numerical model is used to simulate oil movement along the 90-m-long north pool transect from the time of the spill in August 1979 to the approximate time at which core samples were collected in June 1990. The initial condition for the simulation is a hydrostatic water pressure distribution corresponding to a water table altitude computed from water level data collected during sampling from wells 604b and 534b (423.67 m and 423.46 m respectively) in June 1990. The boundary conditions are labeled in figure 4a. The left, bottom, and right boundaries of the domain are assumed to be constant hydrostatic water-pressure boundaries and the oil pressure head is assumed to be 0 m at five infiltration nodes at the top boundary until oil infiltration ceases. Oil infiltration ceases when cumulative oil infiltration is equal to the actual oil mass of 11513 kg as estimated from the measured oil saturation distribution. The oil saturation spatial distributions produced through numerical simulation are visually compared to the observed oil saturation data to determine the most effective modeling scheme.

The effect of heterogeneity on multiphase flow is examined by doing simulations using the following permeability distributions: a uniform mean k (UNIFK); coarse k generated through GSS; and bimodal k produced through IGSIM (figs. 4a, 4b, and 4c). The simulation using UNIFK produces an oil saturation distribution reminiscent of the typical vision of a subsurface oil lens floating on the water table, where the highest oil saturation is located in the middle of the oil body. None of the characteristics of the actual oil saturation distribution that reflect aquifer heterogeneity, such as the high oil saturations in the vadose zone and below the water table, and the irregular oil lens, are reproduced. The simulation using a GSS realization produces a generally uniform oil saturation distribution with oil saturations in the unsaturated zone as high as 0.1 and some variability in the floating oil lens because the heterogeneity within the coarse population is included. Compared to the simulations using UNIFK and GSS permeability distributions, the simulation using an IGSIM realization creates an oil saturation distribution that is most similar to the actual data. The oil lens produced through the IGSIM simulation is highly irregular, with fingering and oil saturations below the water table as high as 0.9. Oil saturations as high as 0.3 are reproduced in the unsaturated zone; however, these high values are not as prevalent as in the data. Due to discrepancies between observed and simulated oil saturation distributions, other factors affecting multiphase flow are being investigated in an effort to more closely reproduce the observed oil distribution.

Two simulations with hysteresis were done using UNIFK and IGSIM k distributions, respectively. Hysteresis has a significant effect on the final oil saturation distribution in the simulation using uniform mean k, but virtually no effect in the simulation using the heterogeneous distribution of k produced through IGSIM. Hysteresis, therefore, is important when aquifer heterogeneity is not properly characterized; the small scale effects of hysteresis are eclipsed when aquifer heterogeneity is adequately represented.

Work in progress involves an investigation of the role of relative permeability in multiphase flow. Simulations are being conducted using the IGSIM k distribution, no hysteresis, recharge, and two different relative permeability relations: Parker (Parker, 1987) and Stone II (Stone, 1973). Preliminary results demonstrate the sensitivity of multiphase flow to relative permeability and reinforce the uncertainty surrounding relative permeability relations and their uniqueness to every individual scenario. The use of the Bemidji field data will lend additional insight on these issues.
Grain-size distribution and permeability estimates from the Bemidji, Minnesota crude-oil-spill site indicate the presence of a bimodal heterogeneity; the two classes correspond to a coarse glacial-outwash sand and interbedded fine-silt lenses. Oil saturation data reveal that this heterogeneity has a significant effect on fluid flow in the subsurface. Geostatistical simulation is conducted in two stages to create a three-dimensional grid of permeabilities that represents the bimodal heterogeneity. A slice of this grid is used as input in a cross-sectional multiphase flow model to analyze the effect of heterogeneity on multiphase flow at the field scale. Three simulations are conducted using increasingly more variable permeability distributions (mean permeability, coarse permeability generated using sequential Gaussian simulation, and bimodal permeability generated using dual sequential indicator and Gaussian simulation). Results of flow simulations using the bimodal permeability distribution generated using dual sequential indicator and Gaussian simulation produce oil saturations that most closely represent the observed oil saturation distribution. The small scale effects of hysteresis are shadowed by the effect of heterogeneity on the oil saturation distribution. The significance of relative permeability in the multiphase flow process at the field scale is currently being investigated.

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Challenges in Detecting Contaminant Effects on an Estuarine Ecosystem Affected by Many Different Disturbances: San Francisco Bay

By Samuel N. Luoma\(^1\), and Frederic H. Nichols\(^1\)

Abstract

The Suisun Bay/Delta at the head of San Francisco Bay is an area where complex factors converge to affect the success of aquatic species. Water diversion and drought have reduced river flows to the bay. The historic elimination of marshes has permanently removed an important source of carbon while river diversion and drought have reduced river-borne inputs of carbon. The invasion of the bay by an exotic clam has affected the abundance of other benthic species and has eliminated previously observed phytoplankton biomass peaks. Coincidentally, populations of important resource species have declined. Persistent contamination in Suisun Bay/Delta accentuates the adverse effects of the above first-order problems. Selenium contamination in benthos is sufficient to affect upper-trophic-level organisms such as birds and fish. Pulse inputs of pesticides occur during high flows. Locations in Suisun Bay were identified that are chronically contaminated with trace organic compounds, cadmium, chromium, and vanadium. At these locations resident bivalves are in poorer condition and have modified reproductive cycles, compared to elsewhere in the estuary. Long-term studies are allowing identification of the relative importance of different factors that disturb biological processes in the estuary. Few multi-disciplinary, long-term field studies are conducted in environments modified by human disturbance. Results from Suisun Bay show how continuity in the study of cause-and-effect may be the only way to separate the influence of the myriad of processes that contribute to ecological characteristics in estuaries.

INTRODUCTION

The array of human activities that have disturbed the San Francisco Bay ecosystem since the gold rush of 1849 are well known (Nichols and others, 1986). However, the effects and relative importance of specific activities are not as well understood.

One focus of the initial phase of the San Francisco Bay toxics program has been the characterization of contamination and its effects in the context of the myriad other disturbances that affect the Suisun Bay and Delta region. In this paper we discuss recent progress in studies of both the natural variability of the Suisun Bay/Delta and effects on aquatic life of human-induced stresses including contaminants.

RIVER FLOW AS A MAJOR DETERMINANT OF ECOSYSTEM FUNCTIONING

The upper San Francisco Bay is a complex estuarine system bounded on its landward side by a tidal freshwater Delta, a highly dissected region of channels and islands at the mouths of the Sacramento and San Joaquin Rivers. The rivers converge at the
eastern end of Suisun Bay, an important nursery area for estuarine fish populations.

Flow from the Sacramento and San Joaquin river system, draining about 40 percent of the land area of California, reflects both the pattern of precipitation over western North America and the operation of the world’s largest man-made water management system (Peterson and others, 1989). More than half of river water flowing toward San Francisco Bay is diverted from the drainage basin through impoundment of snowmelt in reservoirs and pumping of Sacramento and San Joaquin river water from the Delta. The diverted water is consumed in irrigated agriculture and by urban and industrial uses both within and beyond the Bay’s watershed (Nichols and others, 1986). The result is greatly reduced flows into the estuary during spring.

Despite the large-scale water diversion, the estuary typically receives large annual winter/spring pulses of freshwater runoff. Since 1984, however, persistent drought combined with the continuing water diversion to virtually eliminate the annual pulses of freshwater except for an exceptional flood during the spring 1986 (fig. 1).

The reduced flow of freshwater into the estuary has contributed to major changes to the Bay’s ecosystem. As an example, striking declines in the abundance of a number of aquatic species were observed over the last several decades (Jassby and others, 1993a). The mechanisms differ, but reduced river flow seems to have affected the success of a native species of zooplankton, the local mysid shrimp, striped bass, smelt, flounder, and mollusks that inhabit Suisun Bay (Jassby and others, 1993a). The freshwater/seawater interface, as indicated by the geographic location of the 2°/00 isohaline in bottom water, has moved upstream to the detriment of the freshwater organisms that inhabit the region. The reduced flows and upstream movement of salt also have increased the exposure of fish populations to the diversion pumps in the Delta where huge numbers of fish are lost (Jassby and others, 1993a).

Recent studies have demonstrated that reduced river flow also has caused a reduction of organic carbon inflow into the estuary (Jassby and others, 1993b). This work demonstrated that San Francisco Bay has a low input of organic carbon compared to that of many other estuarine systems (Jassby and others, 1993b). Poor light penetration into the silt-laden waters of the Bay limits in situ carbon production by phytoplankton and vascular plants. The extensive marsh system that once existed was also largely eliminated early in this century, reducing carbon inputs from what was once a major source. Thus the rivers are now the remaining important source of carbon input to Suisun Bay/Delta. As river flow was reduced by drought and water diversion, carbon input was reduced concomitantly. The application of isotopic and molecular tracers has revealed that an important source for the organic matter now supporting benthic organisms in the upper estuary is freshwater algae produced in the rivers and Delta (Canuel and others, in preparation). This contrasts to South San Francisco Bay where in situ production is most important (Jassby and others, 1993a).

Another important change in the estuarine ecosystem since the onset of the drought is the disappearance of the summer phytoplankton biomass maximum that typically appeared in the Suisun Bay region (Alpine and Cloern, 1992). This is likely the result of drought-related increases in the abundance of estuarine benthic suspension-feeding organisms, particularly that of a recently introduced Asian clam.

**EFFECTS OF AN EXOTIC SPECIES**

Historically, the most pronounced change to the benthic biota of San Francisco Bay has come from the accidental and intentional introduction of exotic species. Large numbers of sediment-dwelling invertebrates were first introduced during the latter
half of the 19th century with live oysters that were shipped by train from East coast estuaries and transplanted in the bay (Nichols and others, 1986). Exotic invertebrates continue to arrive in the bay in ballast water of cargo ships.

A recent arrival from the estuaries of east Asia, the clam *Potamocorbula amurensis*, has been remarkable in the rapidity with which it became the numerically dominant species throughout the northern part of the estuary and in its potential to change food-web processes (Carlton and others, 1990).

*Potamocorbula* arrived in San Francisco Bay immediately after the major flood of 1986 when most of the estuarine benthic invertebrates were eliminated from the upper estuary because of their intolerance to fresh water. Within months of its first detection in October 1986, *Potamocorbula* became the most abundant benthic organism in Suisun Bay, and has prevented the bottom dwelling species that once dominated during low flow conditions (for example, *Mya arenaria*) from recolonizing the area (Nichols and others, 1990) (fig. 2). The combination of its great abundance and the efficiency with which it filters food particles from the water column has resulted in the near elimination of phytoplankton (diatoms and other microscopic, single-celled plants that form the base of aquatic food chains) from the water of the Suisun Bay region (fig. 2; see Alpine and Cloern, 1992). Further, there is laboratory evidence that *Potamocorbula* eats the juvenile stages of some zooplankton, possibly contributing to the reductions in zooplankton abundance noted during the prolonged drought (Obrebski and others, 1992).

The population biology of *Potamocorbula* has been intensively studied in Suisun Bay, San Pablo Bay and South Bay in monthly samplings between 1989 and the present. Genetic studies (electrophoretic separation of isozymes) indicated *Potamocorbula* had an unusually high within-population genetic variability, contributing to its ability to survive in a range of estuarine conditions (Duda, 1993). A study of its reproductive activity throughout the Bay, under varying salinity, temperature and food regimes, demonstrated major differences in reproductive seasonality between north and south Bay. The animals from Suisun Bay were reproductively active during shorter periods than elsewhere. This difference coincided with, and thus may be related to, spatial differences in food availability and osmotic stress, or possibly contaminant stress. Age structure and condition index (tissue weight of a bivalve of a given shell length) differed among stations in Suisun Bay, and between Suisun and other parts of the estuary. Clams from the upper end of Suisun Bay were generally of longer shell length, had a lower condition index and demonstrated less seasonal fluctuation in condition index than elsewhere (Brown and Luoma, in preparation). Again it is not yet clear whether this is a response to reduced food availability or higher contaminant exposure.

**TRACE ELEMENT CONTAMINATION**

It is probable that contamination from anthropogenic waste discharges is contributing to some of the ecological changes occurring in the upper San Francisco Bay estuary, and biological differences between Suisun Bay and other regions. Recent results of the analysis of sediment cores from San Francisco Bay indicate sediments and water have been contaminated for decades by potentially toxic trace metals (Hornberger and others, in preparation; Van Geen and others, in preparation) and trace organic contaminants (Pereira and others, in preparation; Hostettler and others, in preparation). Industrial and urban development coincided with increased sedimentation during the last 40 years (Fuller, in preparation) and enriched concentrations of Cu, Ag, Pb and Zn. Sediments contaminated for more than one meter in depth are found from Suisun Bay to
Richardson Bay, near the Golden Gate. Pesticides (predominantly DDT) and petroleum by-products are enriched to this depth in Richardson Bay sediments. The Suisun Bay/Delta was characterized by Biggs and others (1989) as one of the estuaries in the United States most susceptible to pollution impact because the physical characteristics of this system limit its natural resilience. River-transported metals, and wastes from nine of the largest point source dischargers in the Bay area are released directly into Suisun Bay (Luoma and others, 1990).

Recent USGS studies illustrate some characteristics of modern organic and inorganic contamination in Suisun Bay. Water soluble pesticides occur periodically in detectable concentrations in Suisun Bay when runoff from agricultural fields reaches the estuary (Kuivila and others, 1996). These pulse inputs from winter storms are superimposed on chronic contamination with petroleum by-products (Pereira and others, 1992) and trace elements (Luoma and others, 1990; Johns and Luoma, 1988; Luoma and others, 1992; Brown and Luoma, in preparation).

Selenium is an example of a chronic contaminant. Field surveys and mass balance calculations (Johns and Luoma, 1988; Cutter, 1989) demonstrated that the most important sources of Se are industrial discharges located near Carquinez Strait. During the low river flows characteristic of the estuary since 1986, Se enrichment in water, suspended particles and benthic species spread throughout Suisun Bay. Substantial Se contamination is found in large fish and in diving ducks in Suisun Bay. The concentrations of Se in water are well below those that cause toxicity in bioassays, but Se concentrations in clams (the food of diving ducks and some fish) are at the level that causes toxicity to birds and fish in food. The combination of studies showed that the contamination of the upper trophic level organisms, and the concomitant threat to their health, resulted from highly efficient transfer of selenite (the form of Se discharged by industry in the area) from water, to phytoplankton and then to clams via ingestion of phytoplankton (fig. 3).

Analysis of *Potamocorbula* tissues has been employed to define chronic trace metal contamination, in addition to selenium. The abundance of this clam across a broad range of salinities in the system makes it an especially suitable organism for spatially comparative studies of contamination. Laboratory studies also showed that *P. amurensis* rapidly bioconcentrates metals in its soft tissues from both food and solution (Brown and Luoma, 1995; Decho and Luoma, 1995). *Potamocorbula* were sampled and analyzed monthly at six stations between January, 1991 and April, 1992, a period of relatively stable river flow. Thus, influences of physical and salinity variability on assessment of source inputs was minimized. A consistent spatial gradient in enrichment with Cd, Cr, Ni, and V was observed in the clam tissues (fig. 4). Concentrations were highest in upper and mid-Suisun Bay and declined through Carquinez Straits into San Pablo Bay. All metals except silver were more enriched in Suisun Bay than in South Bay. The same general gradient in contamination was observed at every sampling time through the 14 month period. Interestingly, the highest

![Figure 3](image_url)

**Figure 3.** An illustration of the concentrations of selenite in micrograms per liter, selenium in suspended particles in micrograms per gram, selenium in clams in micrograms per gram, and the toxicity of selenium in the food of ducks typical of Suisun Bay.

![Figure 4](image_url)

**Figure 4.** Distribution of chromium concentrations in tissues of the clams *Potamocorbula amurensis* and *Corbicula fluminea* in the San Joaquin River, Suisun Bay and San Pablo Bay.
through the 14 month period. Interestingly, the highest concentrations of metals were found in Honker Bay, where no immediate point sources of metal input occur. These data raise the possibility that Honker Bay could be a depositional zone for upper Suisun Bay. Hydrodynamic studies will aid an evaluation of this hypothesis.

INTERACTION OF CONTAMINANTS WITH OTHER DISTURBANCES

The gradient of chronic contamination in Suisun Bay coincides with some of the unique biological characteristics of the area. In *P. amurensis* these include the gradient of lower condition index in Suisun Bay to higher condition index in San Pablo Bay, the lack of a seasonal cycle of condition index in Suisun Bay, and the spatial differences in the seasonality of reproduction in the species. A decline in the condition of a bivalve and alterations to reproductive capabilities can be symptoms of stress in bivalves. Trace elements can cause these responses by disrupting the energetic balance of the organism and reducing energy available for reproduction and growth (Widdows, 1985). On the other hand, food availability and other natural or anthropogenic disturbances can also cause such changes or interact with contaminants in complex ways to produce responses of communities, populations and individuals (Luoma and Carter, 1991).

Ecologists typically cite natural processes or anthropogenically induced changes in habitat conditions to explain differences in populations or declines in fisheries. Toxicologists often search for effects of contaminants where waste discharges from human activities impinge on an aquatic environment. Sufficiently careful, detailed ecological studies that consider contaminants as one of several variables of influence are rare. The studies of 1989 - 1993 identified and specifically characterized ecological and biological anomalies in Suisun Bay. These studies identified several processes that could cause those anomalies, including reduced river flow, lowered carbon inputs, changes in water column ecology caused by invasion of an exotic species, and persistent contamination. Continuity in collection of data that describe these processes, including time series that extend for decades, have previously provided opportunities to distinguish the relative importance of different processes in complex estuarine environments (Jassby and others, 1993a; Nichols and others, 1986). This same approach is the best approach to distinguishing factors that control ecological and biological processes in Suisun Bay.

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Hydrodynamics of California’s Sacramento-San Joaquin Delta, and the Collection of Flow Data for the Tracking of Pesticides

By Richard N. Oltmann

Abstract

The Sacramento and San Joaquin Rivers drain the Central Valley of California where 10 percent of the pesticides used in the United States are applied. The two rivers converge at the head of San Francisco Bay, forming a complex delta consisting of many interconnected sloughs and channels. The tracking of pesticides within and through the delta is difficult because flows are being manipulated constantly and measured-flow data are lacking. Ultrasonic velocity meters and an acoustic Doppler flow-measuring system are being used to collect the flow data necessary to improve understanding of the hydrodynamics of the delta and to track pesticides entering the delta.

INTRODUCTION

Agriculture in the Central Valley of California accounts for 10 percent of the total pesticide usage in the United States. The valley’s two primary river systems, the Sacramento and San Joaquin Rivers (fig. 1), converge to form a large delta at the head of the San Francisco Bay estuary. These two rivers, in addition to a few smaller rivers, discharge almost half of the entire State’s runoff into the delta. A study is currently being done by the U.S. Geological Survey (USGS) to determine how pesticides are transported and transformed as they pass from the valley and through the Sacramento-San Joaquin Delta (Kuivila and Nichols, 1991). The hydrodynamics of the delta are dynamic and complex and not completely understood, primarily because of the lack of measured-flow data. An improved understanding of the hydrodynamics of the delta is needed to study the transport of pesticides through the delta.

DESCRIPTION OF SACRAMENTO-SAN JOAQUIN DELTA AND THE MANIPULATION OF FLOWS

The Sacramento-San Joaquin Delta is about 50 mi east of the city of San Francisco, Calif. (fig. 1). The delta was originally a tidal marsh that experienced floods every winter, very low summer flows, and saltwater intrusion from the bay. The soils of the area are rich, and during the mid-1800’s to early 1900’s levees were built to form islands for agriculture. The delta presently consists of about 1,100 mi of levees, 700 mi of channels, and about 120 flow junctions (fig. 1); the area is about 1,100 mi².

The delta is critical to the State’s water distribution and supply and is an important region for fish and wildlife resources. During normal and wet years, enough precipitation occurs in California to satisfy the state-wide demand for water; however, about two-thirds of the precipitation occurs north of the delta, and about two-thirds of the population and water need is south of the delta. Also, the precipitation occurs during the autumn and winter, and the need is greatest during the hot summer months.

To mitigate these distribution problems, the Federal Central Valley Project (CVP) (construction began in 1930’s) and the State Water Project (SWP) (construction began in 1950’s) were constructed to capture the northern runoff and convey water through the delta to points of need south of the delta. Water is exported from the southern end of the delta by both projects (fig. 1): the CVP delivers water to the San Joaquin Valley primarily for agricultural irrigation, and the SWP delivers water to the southern part of the State through the 500-mi long
Figure 1. Sacramento-San Joaquin Delta and location of ultrasonic velocity meter (UVM) stations and flow routes to export facilities.
California aqueduct. The combined pumping capacity of the projects is about 11,000 ft³/s with an annual mean of about 7,000 ft³/s. In addition, more than 1,800 individual irrigation diversions within the delta can divert as much as 5,000 ft³/s during the height of the irrigation season; annual mean diversion rate is about 1,300 ft³/s. The average flow of the Sacramento and San Joaquin Rivers is 24,000 and 4,600 ft³/s, respectively.

The diversion of water from and within the delta has caused several problems within the estuary, primarily with regard to water quality and fisheries (Miller, 1993). Because the delta supplies drinking water to 20 million Californians, maintaining the quality of delta water is of paramount importance. The diversions greatly reduce the amount of freshwater flowing into the bay from the delta, resulting in increased salt concentrations within the delta—a condition detrimental to drinking-water and irrigation supplies and to aquatic life. The diversions are a possible cause for observed reductions in the abundance of several fish species, some of which are listed or being considered for listing as endangered species. The diversions can affect fish populations by entraining eggs and larvae (some diversions are screened) and by causing cross-delta currents that can confuse spawning fish.

In order to mitigate problems created by the diversions while continuing to export water from the delta, various operating strategies and structural modifications to the delta are used by water managers. A network of real-time, salinity-monitoring stations is operated throughout the delta to monitor water quality. If salinities become too high, additional water is released from upstream storage, water is redirected, and (or) the export rate is reduced to lower the salinity at locations where salinity is high. At times, temporary rock barriers or tidal flap gates are installed across selected channels to prevent the intrusion of brackish water, thus improving the water quality. Barriers also are sometimes temporarily installed in channels near the export facilities to raise the water-surface elevation so that intakes to irrigation pumps remain submerged.

Several operating strategies are used in the delta to mitigate problems to the fisheries. When salmon and striped bass eggs and larvae drift down the Sacramento River, the delta cross channel gates near Walnut Grove (fig. 1) are closed to allow more of the eggs and larvae to move toward the bay and away from the export facilities. The CVP constructed the delta cross channel to transfer Sacramento River water to the Mokelumne River during low- to medium-flow conditions to provide more water to the export facilities in the southern delta; the delta cross channel gates are closed when the flow in the Sacramento River exceeds 25,000 ft³/s. The delta cross channel and Georgiana Slough (fig. 1) are the primary channels for the conveyance of Sacramento River water to the export facilities, and the sum of the two flows is referred to as delta transfer flow. No control structures are on Georgiana Slough; however, consideration is being given to installing a temporary barrier on the slough when eggs and larvae are present in the Sacramento River.

A temporary partial rock barrier is installed each autumn at the head of Old River (fig. 1) near the San Joaquin River during the time when Chinook salmon eggs and larvae are adrift down the San Joaquin River. This barrier allows a greater percentage of eggs and larvae to move north and away from the export facilities. The export rate of the CVP and SWP also can be temporarily reduced or terminated to allow the eggs and larvae to reach the bay. All the above strategies used to control flow complicate the hydrodynamics of the delta and increase the difficulty of tracking pesticides and interpreting pesticide concentration data.

**COLLECTION OF DATA IN THE DELTA AND WHAT HAS BEEN LEARNED FROM THE DATA**

New flow-measuring technology has made it possible to measure flow continuously at key sites in the delta, thus reducing some of the uncertainties about pesticide movement. The USGS is currently collecting flow data in the delta using ultrasonic velocity meters (UVM) and an acoustic Doppler discharge measuring system (ADDMS). A UVM (Laenen, 1985) provides a continuous index velocity, which is measured across a channel between two transducers that are installed at the same depth. The index velocity is correlated to mean cross sectional velocity using measured-flow data collected by the ADDMS. Flow then is computed by multiplying mean cross-sectional velocity and channel cross-sectional area. The ADDMS is a portable system that allows for quick and accurate measurement of discharge as an acoustic Doppler current profiler (Simpson and Oltmann, 1992) is traversed across a channel. Tidal flow measurements of 600-foot-wide channels can be made with the ADDMS in about 3 minutes and without the use of navigational aids.

The USGS has been operating UVM flow stations on the Old and Middle Rivers (fig. 1) in the central delta since January 1987. Old and Middle Rivers are two of the three flow routes by which water is drawn
through the delta to the export facilities in the southern delta. The third route is through upper Old River and Grant Line Canal (fig. 1). Prior to operation of the Old and Middle River UVM's, no continuous flow-monitoring stations were operated in the delta.

The flow data collected at the Old and Middle River stations have improved the understanding of the flow characteristics of the delta. The data show that the tides create a dynamic flow pattern with maximum tidal flows during both flood and ebb of about 10,000 ft³/s during low export periods. Daily mean flows at the flow-monitoring stations indicate that, when a net positive flow exists at the San Joaquin River at Stockton (fig. 1), about 33 percent of the water exported by the projects is drawn down Old River, 45 percent drawn down Middle River, and the remaining 22 percent comes through upper Old River and Grant Line Canal. Net reverse flows can exist on the San Joaquin River at Stockton when the quantity of water drawn to the export facilities through upper Old River and Grant Line Canal exceeds the flow of the San Joaquin River entering the delta from the south. When a temporary partial rock barrier is installed at the head of upper Old River each autumn, the flow percentage increases to 40 percent on the Old River and 52 percent on the Middle River and decreases to 8 percent on the upper Old River and Grant Line Canal.

Near the end of 1992, two UVM stations were installed on the Sacramento River upstream and downstream from Walnut Grove (fig. 1) to provide a measure of delta transfer flow. Two additional stations are planned for installation during 1993 on the Sacramento River downstream from Decker Island and the San Joaquin River at Jersey Point (fig. 1). The sum of flows at the Decker Island and Jersey Point stations will provide a measure of the flow leaving the delta and entering the bay—a quantity commonly referred to as delta outflow. The data provided by the Jersey Point station also will monitor the net reverse flows of the lower San Joaquin River that occur periodically as a result of diversions.

In addition to the above new UVM stations, the cities of Tracy and Stockton (fig. 1) are planning to install UVM stations during 1993 so as to receive National Pollution Discharge Elimination System permits (Darrel Scott, city of Tracy, Calif., oral commun., 1993; Glen D. Birdzell, city of Stockton, Calif., oral commun., 1993). The USGS has been asked to calibrate the stations using the ADDMS.

The ADDMS has been used to make flow measurements at 15-minute intervals over two complete tidal cycles at the western boundary of the delta at Chippis Island (fig. 1) during normal low-flow conditions to measure delta outflow and to determine the range of the tidal flows. The results indicated that the tidal flows were about 300,000 ft³/s during both flood and ebb, with the daily net flows being about 1 to 2 percent of the maximum tidal flows.

Water-level data collected throughout the delta show that during strong spring tides, the mean water elevation of the delta rises about 1 ft above the preceding neap tide level, which is equivalent to about 50,000 acre-ft of water. Whether water is being drawn into the delta from the bay or from upstream sources is not yet clear. Flow data from new and planned UVM stations should help define this process.

The data from all the above UVM stations will be used to calibrate and validate a hydrodynamic model of the delta that the USGS and the California Department of Water Resources (DWR) are currently developing. DWR has been using a model of the delta for several years, but because of the difficulties associated with the collection of flow data in tidal zones, they have not been able to collect sufficient flow data to calibrate and validate the model properly. To supplement the UVM data, the ADDMS will be used periodically to collect 10- to 12-hour time series of flow measurements at critical flow splits in the delta for use in model calibration and validation. Once the calibrated and validated flow and transport models are available, the model will be used to track the movement of dissolved pesticides, as well as other constituents, within and through the delta.

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Diazinon Concentrations and Transport in the Sacramento River and San Francisco Bay, California, February 1993

By Kathryn M. Kuivila and Dwight D. Copeland

Abstract

Previous studies of pesticide concentrations in the Sacramento River suggest that narrow pulses of diazinon, a major dormant spray pesticide, are transported down the river following rainfall. A study in February 1993 followed these anticipated pesticide pulses down the Sacramento River and into San Francisco Bay. Water samples for pesticide analysis were collected daily at four sites in the river and bay. Three distinct pulses of diazinon were detected in the Sacramento River at Sacramento 1 to 3 days after rainfall. The load of diazinon in the Sacramento River in February was calculated to be 340 kilograms (active ingredient) or approximately 0.5 to 1.7 percent of the total diazinon applied to orchards in the Sacramento Valley in January and February. The diazinon pulse detected at Sacramento on February 12 was detected the next day at Rio Vista, 2 days later at Chipps Island (the boundary between the delta and San Francisco Bay), and 3 to 5 days later at Martinez (the western edge of Suisun Bay). Study results suggest that the transport of pesticides from the Sacramento River into San Francisco Bay is episodic and highly dependent on rainfall and flow conditions.

INTRODUCTION

Because of the diverse and extensive use of pesticides in the Sacramento Valley, there is a need for an understanding of pesticide inputs to the Sacramento River and the transport of pesticides in the Sacramento River into San Francisco Bay. Results of previous studies of pesticide concentrations in the Sacramento and San Joaquin Rivers in 1991 and 1992 suggest that rainfall is a major mechanism for transporting dormant spray pesticides from the orchards into the river (unpublished data on file in the California District office of the U.S. Geological Survey). One major dormant spray pesticide is diazinon, an organophosphate insecticide with high water solubility (40 mg/L). Diazinon is applied on almond, peach, and prune orchards in the Sacramento Valley during January and February (California Department of Pesticide Regulation, 1990; Worthing and Hance, 1991).

This report describes the results of a February 1993 study of (1) the temporal variability in diazinon concentrations and loads in the Sacramento River, and (2) the transport of diazinon down the Sacramento River into the northern embayment of San Francisco Bay. This study is part of a research effort to assess quantitatively the fate and transport of pesticides in the river-estuary system.

SAMPLING AND ANALYTICAL METHODS

Four sites were selected along the main flow path of the Sacramento River from Sacramento to the western boundary of Suisun Bay: Sacramento, Rio Vista, Chipps Island, and Martinez (fig. 1). Water samples for pesticide analysis were collected daily at the four sampling locations using a depth-integrating, discharge-weighted sampler (D-77 with a Teflon bottle and nozzle) at either one or three verticals, depending on the site. Flow at the Sacramento site is unidirectional, and sampling studies indicate that the.
Figure 1. Study area and location of streamflow-gaging stations and pesticide sampling sites.
Figure 2. Rainfall at Colusa (shown as bar with amount, in inches per day, above each bar), discharge of the Sacramento River at Freeport, and concentrations of diazinon at Sacramento. Rainfall is recorded from midnight to midnight; ticks represent noon of indicated day.

Pesticides were extracted from filtered 1-L samples onto C₈ solid-phase-extraction cartridges and analyzed using a gas chromatography/ion-trap detector. The reporting limit for diazinon was 15 ng/L. Details of analytical method and quality assurance practices are described by Crepeau and others (1994).

RIVERINE PESTICIDE PULSES

Pulses of diazinon were measured following rainfall in the Sacramento River in previous years; this phenomenon is similar to the spring flush of herbicides observed in surface-water runoff in the midwestern United States (Thurman and others, 1991). The observed riverine pulses of diazinon typically are narrow and well-defined; elevated concentrations can be measured for only a few days to weeks. Diazinon was applied primarily at the end of January 1993 during 2 weeks of dry weather; a series of rainstorms began on February 6. Figure 2 shows the relations among rainfall, discharge, and diazinon concentrations. Rainfall was 0.51, 0.39, and 1.02 in. on February 6, 8, and 9, respectively. A few days after the first rainfall, flow at Freeport increased, reaching a maximum of 52,800 ft³/s on February 14. Similarly, diazinon concentrations increased on February 8 and reached a measured maximum of 393 ng/L on February 12. It rained again on February 20 (1.14 in.), and both discharge and diazinon concentrations soon increased. During this second peak, the diazinon concentrations were 194 ng/L and 186 ng/L on February 21 and 22, respectively. Two days later (February 24), the discharge reached a maximum of 75,400 ft³/s.
Figure 3. Calculated daily diazinon load for the Sacramento River and discharge at Freeport, February 1993. Ticks represent noon of indicated day.

Traveltimes were estimated by calculating velocities for discrete reaches of the river from a regression relation between measured instantaneous velocity and the logarithmic of instantaneous discharge for the cross section (at streamflow-gaging stations shown in fig. 1) for the selected time period. Most of the orchards are near Colusa, north of Sacramento, in a narrow band along the Sacramento River or clustered along the Feather River, a tributary that enters the Sacramento River 20 rm upstream from Sacramento. The estimated traveltame after the February 9 rainfall from Colusa down the Sacramento River to the city of Sacramento (89.4 rm) was 1 1/2 days. This traveltame estimate is low because the calculation does not include transport time from the field to the river and velocities were slower along the Feather River than along the Sacramento River. The observed lag between rainfall and peak pesticide concentrations was 3 days. The lag between the second rainstorm on February 20 and the corresponding peak diazinon concentration was much shorter (1 day). The discharge measured on February 20 (58,800 ft³/s) was almost double the discharge measured on February 9 (32,000 ft³/s), indicating increased stream velocities, which probably shortened traveltimes on February 20. Increased soil-moisture content resulting from infiltration of precipitation from the February 9 and 20 rainfalls may have shortened traveltime from fields to river.

CALCULATION OF DIAZINON LOADS

Diazinon loads for the Sacramento River were calculated by multiplying the instantaneous measured pesticide concentration by the tidally filtered, daily mean discharge (fig. 3). The integrated loads for each peak were 163 kg for February 8-16, 129 kg for February 19-25, and 30 kg for February 25-28. Although the maximum concentration during the second peak (194 ng/L) was only half that during the first peak (393 ng/L), the load of diazinon in the river was similar during the two peaks. In contrast, the maximum concentration (79 ng/L) and calculated diazinon load (30 kg) were lower during the third peak than during the previous two peaks, possibly because the amount of diazinon transport from orchards decreased.

The total load of diazinon in the Sacramento River was calculated and compared with the amount of diazinon applied to orchards in the Sacramento Valley. During February, the total load was 340 kg. The most recent diazinon-use data available is for 1990 (California Department of Pesticide Regulation, 1990), when 19,900 kg (active ingredient) was applied in January and February of that year. In addition, diazinon has replaced an unknown portion of the previously used ethyl parathion (now banned) (51,300 kg active ingredient). Therefore, assuming a maximum 1:1 replacement of ethyl parathion by
diazinon, from 19,900 to 71,200 kg of diazinon was applied to orchards in the Sacramento Valley in 1993. In this context, the calculated load in the Sacramento River at Sacramento represents 0.5 to 1.7 percent of the amount applied in January and February. These results support the findings of Wauchope (1978), who reported that pesticide losses in runoff from agricultural fields were up to 0.5 percent of the amounts applied, unless heavy rainfall fell within 1 to 2 weeks after application.

PESTICIDE TRANSPORT INTO SAN FRANCISCO BAY

A main flowpath of water down the Sacramento River is along the ship channel past Rio Vista, Chipps Island, and Martinez (fig. 1). The first pulse of diazinon in the Sacramento River was followed from Sacramento through Suisun Bay (the northern embayment of San Francisco Bay) (figs. 1 and 4). Initially detected at Sacramento, the diazinon concentrations reached a maximum value of 393 ng/L on February 12 (figs. 3 and 4). This pulse was detected at Rio Vista (43 rm downstream from Sacramento) on February 13; the maximum concentration was 300 ng/L. Two days later (February 15), the pulse was detected at Chipps Island (16.5 rm from Rio Vista); the maximum concentration was 200 ng/L. Finally, diazinon concentrations of 100 and 120 ng/L were detected on February 18 and 20 at Martinez (14.5 rm seaward from Chipps Island). The approximate traveltime was 1 day from Sacramento to Rio Vista, 2 days from Rio Vista to Chipps Island, and 3 to 5 days from Chipps Island to Martinez. As the pesticide pulse moved seaward, the maximum concentration decreased and the pulse dispersed over time, in part because of tidal diffusion.

The National Academy of Sciences and National Academy of Engineering (1973) recommended a guideline of 9 ng/L as a maximum diazinon concentration in surface water for the protection of freshwater aquatic life; the International Joint Commission (1975) suggested a limit of 8 ng/L. Currently, the U.S. Environmental Protection Agency has not established an aquatic-life water-quality criterion for diazinon. All the water samples collected at the four study sites in February 1993 contained diazinon concentrations above the recommended guidelines for protection of aquatic life. In addition, other pesticides besides diazinon were present in the water samples during these runoff events (data not shown), and additive or synergistic effects can increase the total toxicity of the water.

Figure 4. Concentrations of diazinon in the Sacramento River at Sacramento, Rio Vista, Chipps Island, and Martinez, February 1993. Ticks represent noon of indicated day.
SUMMARY AND CONCLUSIONS

The results of this study and previous studies show that rainfall affects the transport of pesticides from orchards into rivers. Each rainstorm in February 1993 was followed by elevated concentrations of diazinon in the Sacramento River at Sacramento. Under high-flow conditions, diazinon was transported down the Sacramento River and into San Francisco Bay in distinct pulses. The concentrations measured in the river and bay during this study exceed recommended water-quality guidelines for freshwater aquatic life.

REFERENCES

California Department of Pesticide Regulation, 1990, Pesticide use data—Computer tapes available from California Department of Pesticide Regulation, Sacramento, Calif. 95814.
Distribution and Possible Biological Effects of Diazinon in the San Joaquin River and the Sacramento-San Joaquin Delta, California, February 1993

By Kathryn M. Kuivila¹, Robert C. Sheipline¹, and Christopher G. Foe²

Abstract

The distribution and possible biological effects of a dormant spray pesticide, diazinon, were examined by measuring pesticide concentrations and estimating toxicity by means of bioassays at a series of sites in the Sacramento-San Joaquin Delta. A double peak of diazinon concentration was observed in early February 1993 at Vernalis on the San Joaquin River after heavy rains; similar pulses were detected at Stockton 2 days later. Two geographically separate sources of diazinon--orchards along the western side of the San Joaquin River near Patterson and orchards along the Merced River--could account for the observed pattern of diazinon concentrations in early February. Distributions of diazinon at central delta sites on Old and Middle Rivers were not pulselike; instead, the concentrations steadily increased during the sampling period. Seven-day bioassays indicated that San Joaquin River water at Vernalis was acutely toxic to *Ceriodaphnia dubia* (water flea) for the 12 consecutive days (February 8-19) with the highest diazinon concentrations. Examination of 96-hours LC₅₀ values (lethal concentration that kills 50 percent of test organisms in 96 hours) indicates that measured diazinon concentrations could not account for all the observed toxicity. Other pesticides present could contribute to the toxicity.

INTRODUCTION

The biological effects of dormant spray pesticides used on orchards in the San Joaquin River Basin are of environmental concern (Foe and Connor, 1991; Foe and Sheipline, 1993). Diazinon, an organophosphate insecticide, is the primary dormant spray applied in January and February on almond, apple, apricot, cherry, and peach orchards in the San Joaquin River Basin (California Department of Pesticide Regulation, 1990). Distinct high-concentration pulses of diazinon have been detected in the San Joaquin River in January and February 1991 and 1992 following rainfall (unpublished data on file in the California District office of the U.S. Geological Survey). The results of bioassay surveys indicate that San Joaquin River water containing elevated concentrations of dormant spray pesticides, including diazinon, is generally toxic to *Ceriodaphnia dubia* (water flea) (Foe and Connor, 1991).

This report summarizes the results of a study on the distribution of diazinon concentrations in the San Joaquin River and Sacramento-San Joaquin Delta during February 1993 and assesses the potential biological effects of the diazinon-laden water. This study is part of a research effort to understand the fate and transport of pesticides in the river-estuary system.

SAMPLING AND ANALYTICAL METHODS

The sampling approach was to measure pesticides and toxicity at four sites along a flow path from Vernalis through Stockton to the export pumps: Vernalis (at the mouth of the San Joaquin River), Stockton, Old River, and Middle River (fig. 1). Water samples were collected at Vernalis twice a day using a depth-integrating, discharge-weighted sampler (D-48) at a single vertical from a bridge. Flow at this site is unidirectional, and sampling studies indicated that the composition

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EXPLANATION

▲ Streamflow gaging station
▼ Pesticide sampling site

Figure 1. Study area and location of streamflow-gaging stations and pesticide sampling sites.
and concentrations of dissolved constituents at a single vertical is representative of the cross section under most flow conditions (data not shown). Discharge was also recorded at Vernalis, a streamflow-gaging station. In contrast to the Vernalis site, flow at the Stockton, Old River, and Middle River sites reverses during the tidal cycle. Flow and solute concentrations do not necessarily covary over time within a tidal regime; therefore, extensive sampling during the tidal cycle would be necessary to calculate constituent loads. Instead, samples were collected at slack after ebbtide at Stockton and at slack after floodtide at the Old and Middle River sites (see Oltmann, 1996, for additional details of delta hydrodynamics). This sampling scheme was designed to estimate the most forward movement of solutes along a flow path through the delta and to enable a comparison of daily concentrations in the delta.

One of the water samples collected at Vernalis each day during February was split for analysis of dissolved pesticides and for bioassays. The other water sample from Vernalis and the daily water samples from the other three sites also were analyzed for dissolved pesticides. Filtered 1-L samples were extracted using C₈ solid-phase extraction cartridges, and the pesticides were analyzed using a gas-chromatograph/ion-trap detector. The reporting limit for diazinon was 15 ng/L.

Seven-day C. dubia bioassays (U.S. Environmental Protection Agency, 1989) were done at the Sierra Foothill Laboratory. All tests met the U.S. Environmental Protection Agency (USEPA) bioassay acceptance criteria of at least 80-percent control survival. A water sample was considered toxic if test organism mortality was 30 percent or greater than the associated laboratory control mortality.

DIAZINON CONCENTRATIONS IN THE SAN JOAQUIN RIVER

In 1993, most of the diazinon was applied to orchards during 2 weeks of dry weather at the end of January (Elizabeth Deaver, San Joaquin County Department of Agriculture, oral commun., 1993). Both streamflow and diazinon concentration in the San Joaquin River began to increase immediately at Vernalis on February 8 in response to the first rainfall on February 8 and 9–0.59 and 1.29 in. of rain, respectively. Two well-defined peaks of diazinon concentration were detected; the first had a maximum concentration of 773 ng/L at 2400 hours on February 8 and the second had a maximum concentration of 1,071 ng/L at 1900 hours on February 11 (fig. 2). Differences in traveltimes to Vernalis from two geographically separate sources could have resulted in the observed double pulse after a single rainfall event.
Toxicity of San Joaquin River water in January and February has been attributed to the presence of dormant-spray orchard pesticides, including diazinon. Diazinon is applied to orchards located primarily in two areas in the San Joaquin drainage basin--along the western side of the San Joaquin River near Patterson (26 rm upstream of Vernalis) and along the Stanislaus, Tuolumne, and Merced Rivers on the eastern side of the San Joaquin River (California Department of Pesticide Regulation, 1990). Analysis of bioassays using C. dubia from 1988 through 1990 showed a pattern of high invertebrate toxicity in the San Joaquin River between the confluence of the Merced and Stanislaus Rivers, much lower toxicity in the San Joaquin River upstream of the confluence of the Merced River, and no recorded toxicity in the Stanislaus River (Foe and Connor, 1991).

Runoff in agricultural drains and creeks on the western side of the San Joaquin River responds rapidly to rainfall (J.L. Domagalski, U.S. Geological Survey, oral commun., 1993) and could be the source of the first diazinon peak concentration detected on February 8. In contrast, agricultural runoff from orchards located along the Merced River has a much longer traveltime to Vernalis than runoff from the western drains and could be the source of the later diazinon peak concentration detected on February 11.

Traveltime was estimated by calculating velocities for discrete reaches of the river from a regression relation between measured instantaneous velocity and the logarithm of instantaneous discharge for the cross section (at streamflow-gaging stations shown in fig. 1) for the selected time period (Clifton and Gilliom, 1989). Because early February was a time of unsteady flow and the actual time that runoff containing peak diazinon concentrations entered the river is not known, the traveltime estimates are expressed as a range. The estimated traveltime along the San Joaquin River from Patterson to Vernalis was 19 to 27 hours. In contrast, the estimated traveltime from the area of orchards around the Merced River (approximately 24 rm upstream of the confluence with the San Joaquin River) to Vernalis along the Merced and San Joaquin Rivers was 55 to 74 hours. The two observed diazinon peaks were separated by 2 1/2 days at Vernalis. This difference in arrival time supports the hypothesis of two sources of diazinon runoff--orchards along the western side of the San Joaquin River near Patterson and orchards farther upstream along the Merced River.

During high-flow conditions, such as occurred in January and February 1993, there is positive net flow along the San Joaquin River toward Stockton (Oltmann, 1996). High concentrations of diazinon, similar to those observed at Vernalis (on February 8, 11, and 19), also were detected at Stockton 2 days later (on February 10, 13, and 21) (fig. 3). Because flow reverses within the delta, insufficient data are available to estimate time of travel from Vernalis to Stockton.

In the central delta, water from the Sacramento, Mokelumne, and San Joaquin Rivers mixes in a series of complex channels and is subjected to tidal flow reversals (Oltmann, 1996). During the same time period that diazinon pulses were observed at Vernalis, similar diazinon pulses (as high as 393 ng/L) were detected in the Sacramento River (Kuivila and Cope-land, 1994). Well-defined pesticide pulses were not observed at the Old and Middle River sites because of
the two riverine sources of diazinon and the hydrodynamic complexity of the delta; instead, the diazinon concentrations steadily increased through February (fig. 3).

**POTENTIAL BIOLOGICAL EFFECTS ON THE DELTA**

The results of this pesticide study are useful to estimate the possible effects of dormant spray pesticides, particularly diazinon, on the ecology of the delta. The National Academy of Sciences and National Academy of Engineering (1973) has recommended a guideline of 9 ng/L diazinon as a maximum concentration in surface water for protection of aquatic life. The International Joint Commission (1975) suggests a similar guideline of 8 ng/L diazinon for the Great Lakes. Currently (1993), there is no USEPA aquatic-life criterion for diazinon.

Bioassays were used to determine the potential biological effects of river water contaminated with dormant spray pesticides (U.S. Environmental Protection Agency, 1989; 1991). One hundred percent *C. dubia* mortality was observed in water samples collected for 12 consecutive days (February 8-19) from the San Joaquin River at Vernalis. The bioassay mortality corresponded with the highest diazinon concentrations (fig. 2 and table 1). Conversely, no toxicity was observed in water collected before (February 5 and 7) or after (February 20-25) the peaks of diazinon concentration.

Ambient diazinon concentrations appear sufficiently elevated to contribute to, but not explain all, the *C. dubia* mortality. The laboratory 24- to 96-hour LC₅₀ values for *C. dubia* were between 430 and 550 ng/L of diazinon. In 7-day tests, concentrations of 120 ng/L of diazinon did not result in mortality, but did result in a 25-percent reduction in reproduction (Foe and Sheipline, 1993). In the San Joaquin River, water samples with diazinon concentrations higher than 350 ng/L resulted in 100 percent mortality in 48 hours, and samples with diazinon concentrations of 148 to 263 ng/L resulted in 100 percent mortality in 7 days (table 1). No *C. dubia* toxic response—that is, mortality at or greater than 30 percent—was measured for diazinon concentrations at or below 84 ng/L. Chlorpyrifos, methidathion, and carbaryl were routinely detected in the water samples (table 1), and other pesticides also could have been present. Some or all these pesticides could have acted together either addictively or synergistically to produce the observed toxicity.

### Table 1. Vernalis bioassay results and pesticide data

<table>
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<th>Other pesticides detected</th>
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<td>42</td>
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</table>

1Mortality occurred within 48 hours.
2Mortality occurred within 7 days.

The ecological effects of pulses of pesticides on aquatic biota in the delta are not known. However, most freshwater zooplankton (copepods, rotifers, and cladocerans) in the delta are in decline (Obrebski and others, 1992), the cause is unknown. The bioassay and pesticide data indicate that dormant spray pesticides enter the delta from the San Joaquin River in concentrations that can affect select organisms.

### SUMMARY

Distinct pesticide pulses, with high concentrations of diazinon, were detected at Vernalis on the San Joaquin River after rainfall in February 1993. A double peak of diazinon observed in early February could be from two sources; this hypothesis was supported by traveltime estimates. Pesticide pulses were observed at Stockton 2 days later than at Vernalis; in contrast, the diazinon concentrations at Old and Middle Rivers increased steadily over time. San Joaquin River water containing the highest diazinon concentrations also was the most toxic to *C. dubia* in bioassay tests. Published LC₅₀ values indicate that the observed
diazinon concentrations could account for only some of the observed toxicity. More extensive chemical and toxicological testing needs to be done to ascertain the chemicals responsible for causing toxicity, to determine their distribution and fate within the delta, and to evaluate their effect on native organisms.

REFERENCES

California Department of Pesticide Regulation, 1990, Pesticide use data: Computer tapes available from California Department of Pesticide Regulation, Sacramento, Calif.


Concentrations of Dissolved Rice Pesticides in the Colusa Basin Drain and Sacramento River, California, 1990-92

By Kathryn L. Crepeau¹, Kathryn M. Kuivila¹, and Joseph L. Domagalski¹

Abstract

The measured concentrations of rice pesticides in the Colusa Basin Drain and the Sacramento River, California, decreased during 1990-92. Molinate, carbofuran, and thiobencarb are applied to the Sacramento Valley ricefields in April, May, and June. These pesticides are of concern because of the potential effect of discharge water from ricefields on striped bass larvae. Concentrations of dissolved pesticides from ricefields were measured at the Colusa Basin Drain (a major source of ricefield drainage) and the Sacramento River at Sacramento, Rio Vista, and Chipps Island during May, June, and July each year. The highest pesticide concentrations were measured at the Colusa Basin Drain with progressively decreasing concentrations downstream, principally because of dilution. During 1990-92, the maximum molinate concentration in the Colusa Basin Drain decreased by a factor of three each year. The maximum carbofuran concentration decreased by a factor of four during 1990-91. In contrast, the maximum carbofuran and thiobencarb concentrations in 1992 remained at the 1991 concentrations. The holding time before ricefield water could be discharged into the Sacramento River increased yearly during 1990-92. This allowed further degradation of the pesticides and resulted in the decreased concentrations of pesticides measured in the Colusa Basin Drain water and downstream sites.

INTRODUCTION

Rice is a major crop grown in the Sacramento Valley, California; as many as 500,000 acres are harvested each year (California Regional Water Control Board, Central Valley Region, 1991a). The ricefields are flooded with irrigation water from the Sacramento River a few days before seeding in April or May. Pesticides can be incorporated into the soil before flooding or applied by air after flooding and seeding. Field water returned to the Sacramento River through the Colusa Basin Drain (CBD) (fig. 1) can contain rice pesticides. These pesticides are of concern because of their potential effect on striped bass larvae in the Sacramento River (California Regional Water Quality Control Board, 1991a). The striped bass spawn between early May and mid-June, the time of ricefield water discharge.

Several pesticides are applied to rice in the Sacramento Valley; however, three pesticides of concern for water quality are molinate, carbofuran, and thiobencarb. Molinate, a thiocarbamate herbicide used on rice to control broad-leaved and grassy weeds, is applied usually from the air 7 to 10 days after seeding. The water solubility of molinate is 800 mg/L (milligram per liter). In shallow ricefields, molinate is lost through volatilization (Soderquist and others, 1977) because of molinate's high vapor pressure [410 mPa (millipascal) at 20 °C (degree Celsius)]. In addition, molinate undergoes photolysis to form 2-keto molinate and 4-keto molinate. The quantity of molinate [1,492,300 lb (pound)] used on rice in the Sacramento Valley was more than 15 times greater than the quantity of carbofuran (88,240 lb) or thiobencarb (95,830 lb) during 1990 (California Department of Pesticide Regulation, 1990). Carbofuran, a carbamate insecticide used to control the rice water

Figure 1. Pesticide sampling sites in the Sacramento Valley, California.
weevil, is incorporated into the soil as a granular formulation prior to planting or applied by air after flooding. Carbofuran’s water solubility and vapor pressure are 700 mg/L (25 °C) and 2.7 mPa (33 °C), respectively. In irrigation water, the half-life of carbofuran ranges from 18 to 25 days (Nicosia, 1989) with the primary degradation processes being abiotic hydrolysis (Sharom and others, 1980) and microbial degradation (Chaudry and Ali, 1988). Thiobencarb, a thiocarbamate herbicide used to control grassy weeds, particularly barnyard grass, is applied by air when rice is at the two-leaf stage (California State Water Resources Control Board, 1984). Thiobencarb’s water solubility and vapor pressure are 30 mg/L (20 °C) and 2 mPa (20 °C). The primary loss of thiobencarb is through photolysis (Crosby, 1983).

This paper presents the results of sampling done in the Colusa Basin Drain and Sacramento River during May, June, and July of 1990, 1991, and 1992 and discusses the effects of degradation and dilution processes on the concentration of rice pesticides.

METHODS

The CBD and the Sacramento River sites were sampled each year during May, June, and July. Water was collected using a depth-integrating sampler, such as a D-77 (Edwards and Glysson, 1988, p. 13-14). The sample volume ranged from 100 mL (milliliter) to 4 L (liter), depending on the site and estimated pesticide concentration.

The samples were filtered through a 0.7 μm (micrometer) glass-fiber filter prior to extraction using C-8 solid-phase extraction cartridges. The water was pumped through the cartridge at a rate of 20 mL/min. Terbuthylazine was added to the filtered sample to check the extraction efficiency of the cartridge. The mean accuracy (percent recovery) and the relative standard deviation for molinate, carbofuran, and thiobencarb are 70.1± 22.2, 71.6± 35.1, and 56.2± 17.2. The cartridges were dried by positive pressure of high-purity carbon dioxide to remove all the interstitial water. Dried cartridges were eluted with hexane ether mixture (1:1 ratio) and evaporated to 200 μL. The samples were analyzed using a gas chromatograph with an ion trap detector. The detection limits for the 1990 analyses were 0.100 μg/L for molinate, 0.050 μg/L for carbofuran, and 0.025 μg/L for thiobencarb. The analytical sensitivity was increased in 1991 (0.030 μg/L for molinate and 0.015 μg/L for carbofuran).

RESULTS AND DISCUSSION

The maximum pesticide concentrations at the CBD and Sacramento River sites decreased each year during 1990-92. The molinate, carbofuran, and thiobencarb concentrations at CBD are shown in figure 2. The maximum concentration of molinate decreased from 51 μg/L in 1990 to 14.9 μg/L in 1991 and to 4.10 μg/L in 1992, a decrease of about a factor of three each year. The average percent recovery and standard deviation for molinate are 95.8± 8.2 (Daniel Killingsworth, Zeneca Ag Products, written commun., 1990). For carbofuran, the maximum concentration measured in 1990 was 1.1 μg/L (California Regional Water Quality Control Board, Central Valley Region, 1991b). This data set had a higher carbofuran detection limit (0.50 μg/L); thus, carbofuran was not detected in most of the 1990 samples. The average percent recovery and relative standard deviation for carbofuran was 93± 14 (Smith, 1990). The maximum carbofuran concentrations were similar for 1991 and 1992 (0.308 μg/L and 0.229 μg/L, respectively). Overall, the maximum carbofuran concentration decreased by a factor of four from 1990 through 1991, but changed slightly from 1991 through 1992. With the higher detection limit in 1990 (0.10 μg/L), thiobencarb was not detected in any of the samples at CBD (California Regional Water Quality Control Board, Central Valley Region, 1991b). The average percent recovery and standard deviation for thiobencarb was 97.7± 11.8 (Daniel Killingsworth, Zeneca Ag Products, written commun., 1990). The maximum thiobencarb concentration was 0.162 μg/L in 1991 and 0.200 μg/L in 1992, again with no appreciable change in concentration during 1991-92.

The State of California’s regulations for the release of ricefield water has required progressively longer holding times in recent years. The increase in holding time for ricefield water from 1990 to 1992 with carbofuran application was zero to 24 days, with molinate was 19 to 28 days, and with thiobencarb has remained at 30 days. The increase in holding time allows for further degradation and volatilization of the pesticides in the ricefields. The shallow ricefields provide a large surface area and warm temperatures (greater than 30 °C) for volatilization. As a mechanism for loss, volatilization is important only for
Figure 2. Concentrations of molinate, carbofuran, and thiobencarb measured at Colusa Basin Drain, California, 1990-92. The 1990 data for molinate were obtained from California Regional Water Quality Control Board, Central Valley Region, 1991b.
molinate because molinate vapor pressure is high, more than 100 times greater than the vapor pressure for carbofuran or thiobencarb. Photolysis, an important degradation mechanism for molinate and thiobencarb, is enhanced by the large surface area of the ricefields. The photodegradation products for molinate, 2-keto and 4-keto molinate, were present in the CBD and Sacramento River samples (Domagalski and Kuivila, 1991). In contrast, carbofuran degradation occurs primarily by abiotic hydrolysis and microbial degradation. These degradation processes are enhanced by pH values greater than 7 and warm temperatures that prevail in the ricefield water (Crosby, 1983). The measured decreases in pesticide concentration during 1990-92 can be attributed to the increased holding times for ricefield water.

The measured concentrations of molinate and carbofuran at each of the sampling sites for 1991 are shown in figure 3. The highest concentrations were measured at the CBD with progressively decreasing concentrations downstream. The maximum concentration for molinate decreased from 14.9 μg/L at CBD to 1.17 μg/L at Sacramento to 0.347 μg/L at Rio Vista. The maximum concentration for carbofuran decreased from 0.308 μg/L at CBD to 0.086 μg/L at Sacramento to 0.038 μg/L at Rio Vista. The maximum concentration of thiobencarb measured in 1991 at CBD was 0.162 μg/L (fig. 2). Thiobencarb was not detected at the Sacramento River sites at Sacramento or Rio Vista in 1991.

The decrease in pesticide concentration downstream was caused primarily by dilution and degradation. The greatest dilution was between CBD and the Sacramento site after the release of ricefield discharge water into the high volume Sacramento River. The maximum contribution of ricefield discharge water to the total flow of the Sacramento River is about 30 percent (California State Water Resources Control Board, 1984). The decrease in maximum concentrations of molinate and carbofuran from CBD to Sacramento in 1991 was by a factor of about 12 and 4, respectively. The thiobencarb concentration decreased from 0.162 μg/L to less than 0.025 μg/L, a factor of 6 or greater. If the decrease in carbofuran concentration is attributed entirely to dilution, the greater decrease in molinate and thiobencarb concentrations can be attributed to degradation. Photolysis and volatilization of molinate and thiobencarb occur more readily in CBD than in the Sacramento River because of the higher temperatures and the higher surface area to volume ratio of the CBD compared to the Sacramento River.

The decrease in pesticide concentrations from the Sacramento to the Rio Vista sites apparently is caused primarily by dilution, because the patterns of decrease in molinate and carbofuran from the Sacramento to Rio Vista sites are similar. Because channel depths increase with a reduction in surface area to volume ratios, photolysis and volatilization of molinate in the river probably are not as important as in the shallow agricultural drains. Water samples for pesticides were collected at Chipps Island in 1990 and 1991. Molinate, carbofuran, and thiobencarb concentrations measured on June 5, 1990, were 0.410 μg/L, 0.089 μg/L, and 0.044 μg/L, respectively. In 1991, the molinate concentrations measured were 0.083 μg/L (July 25) and 0.073 μg/L (August 1); carbofuran and thiobencarb were not detected (detection limits for carbofuran and thiobencarb were 0.015 μg/L and 0.025 μg/L, respectively).

Toxicity of the rice pesticides to aquatic life in the Sacramento River has been a concern (California Regional Water Quality Control Board, Central Valley Region, 1991a). The acute toxicity of carbofuran is greater than that of molinate or thiobencarb. Annual water-quality performance goals of the California State Water Resources Control Board are daily maximums and apply to all freshwater environments. The 1992 performance goals reflect the comparatively high acute toxicity of carbofuran; the performance goal is 0.4 μg/L for carbofuran contrasted to 10 μg/L for molinate and 1.5 μg/L for thiobencarb (California Regional Water Quality Control Board, Central Valley Region, 1993). All rice-pesticide concentrations measured in 1992 during this study were less than these performance goals. The increased holding time for ricefield water has apparently been successful in decreasing the rice pesticide concentrations in the CBD and Sacramento River. However, it is important to note that these performance goals are based on the toxicity of a single pesticide. In the natural environment, aquatic organisms commonly are exposed to several pesticides at the same time, which can create additive or even synergistic toxic effects.

**SUMMARY**

During 1990-92, the maximum molinate concentration measured in the CBD has decreased by a factor of three each year. Carbofuran concentrations
Figure 3. Concentrations of (A) molinate and (B) carbofuran measured at Colusa Basin Drain and the Sacramento River at Sacramento and Rio Vista, California, 1991.
Figure 3. Concentrations of (A) molinate and (B) carbofuran measured at Colusa Basin Drain and the Sacramento River at Sacramento and Rio Vista, California, 1991—Continued.
decreased similarly from 1990 through 1991, but decreased only slightly from 1991 through 1992. Thiobencarb had no appreciable change in concentrations measured during 1991-92. The decreases in pesticide concentration can be attributed to degradation and loss by volatilization in the ricefield as a result of increased holding times of irrigation water. The pesticide concentrations decreased downstream from the CBD along the Sacramento River. Dilution seems to be the primary cause of the decreasing pesticide concentrations. However, between CBD and Sacramento, the molinate and thiobencarb concentrations decreased more than the carbofuran concentration, indicating that further loss of molinate and thiobencarb probably occurred in the CBD by photolysis and volatilization.

REFERENCES

California Department of Pesticide Regulation, 1990. Pesticide use data: Computer tapes available from California Department of Pesticide Regulation, Sacramento, CA 95814.


Method for Estimating the Activity of Carbofuran-Degrading Microorganisms in Environmental Samples

By William J. Meyers and Kathryn M. Kuivila

Abstract

A method was developed to determine the presence and activity of carbofuran degrading organisms in aqueous field samples. Carbofuran is a broad spectrum systemic insecticide used on rice in the Sacramento Valley of California. Following the release of treated rice irrigation water, concentrations of carbofuran can be detected in agricultural drains and in the Sacramento River. Microbial populations influence the degradation rate of carbofuran in soils, but little is known about the importance of these organisms in the degradation of carbofuran in aqueous systems. The method described uses laboratory-scale microcosms containing an environmental culture and carbon-14 (\(^{14}\)C) ring-labeled carbofuran to evaluate the ability of microorganisms to degrade carbofuran. Degradation is indicated by the evolution of \(^{14}\)C-carbofuran-7-phenol and carbon-14-carbon dioxide (\(^{14}\)C-CO\(_2\)). Ethyl acetate was used to extract the \(^{14}\)C ring-labeled compounds from aqueous solution. \(^{14}\)C-carbofuran was resolved from \(^{14}\)C-carbofuran-7-phenol by means of thin layer chromatography, and the \(^{14}\)C quantified using a radioisotope plate reader. Sodium hydroxide base traps were used to capture the \(^{14}\)C-CO\(_2\) evolved from the cultures and quantified using a scintillation counter. The method was tested using three different aqueous cultures. Overall recoveries of \(^{14}\)C were 66.8 percent plus or minus 6.3 percent at 95-percent confidence interval (n=24).

INTRODUCTION

Pesticides are applied to ricefields of the Central Valley of California to prevent the growth of plants, algae, and insects that reduce rice yields. Rice growers are required to retain treated irrigation water on the field following pesticide application to promote dissipation before releasing the water into agricultural drains that discharge into the Sacramento River. During the spring and summer months, rice return flows can account for as much as 30 percent of total flow in the Sacramento River (California State Water Resources Control Board, 1984). Therefore, the water quality of the Sacramento River and the Sacramento-San Joaquin Delta can be greatly affected by the quality of rice return water. Pesticide inputs into the river have been identified as a possible cause of the recent decline in the striped bass population (Phillips, 1987). Acute and chronic toxicity tests using rice return water implicate carbofuran as one of the compounds causing toxicity to the freshwater invertebrate Ceriodaphnia dubia (Norberg-King and others, 1991).

Carbofuran (2,2-dimethyl-2,3-dihydrobenzofuranyl-7-N-methyl carbamate) is a broad spectrum systemic insecticide used on a wide variety of crops in the United States. The Sacramento Valley—the northern third of the Central Valley of California—is one of the principal rice producing areas in the United States with as many as 500,000 acres in production annually (California Regional Water Control Board, Central Valley Region, 1991). In 1990, about 40,000 kg of carbofuran were used in the Sacramento Valley to control the rice water weevil (California Department of Pesticide Regulation, 1990). Despite preventive measures to dissipate this insecticide, concentrations of carbofuran have been detected in the Sacramento River. The results of a Lagrangian sampling study (Domagalski and Kuivila, 1991) indicate that carbofuran then can be transported conservatively down the Sacramento River.

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The influence of microbial populations on the degradation of carbofuran in soils has been well documented (Harris and others, 1988; Parkin and Shelton, 1992), but little is known about the importance of these organisms in the degradation of carbofuran in aqueous systems. This paper describes a microcosm method that was developed to determine the presence of carbofuran-degrading organisms in aqueous field samples and to estimate the importance of these organisms in the degradation of carbofuran. The paper was prepared as part of the San Francisco Bay Toxic Contaminants Study.

The degradation products of carbofuran have been well characterized (Metcalf and others, 1968). The carbamate moiety is very susceptible to alkaline hydrolysis, producing carbofuran-7-phenol (fig. 1).

$$\text{CO} + \text{H}_2\text{O} \rightarrow \text{OH}$$

Figure 1. Main degradation products of (I) carbofuran. Structure (II) is carbofuran-7-phenol. The main products of abiotic hydrolysis (H) and microbial degradation (M) are indicated.

Microorganisms also can hydrolyze carbofuran to produce carbofuran-7-phenol and may be able to use the carbamate moiety as a sole source of nitrogen (Karns and others, 1986; Chaudry and Ali, 1988). Microbial activity in soil can result in an accumulation of carbofuran-7-phenol (Harris and others, 1984; Rajagopal and others, 1984; Chapman and others, 1985). Organisms also have been isolated that use carbofuran as a sole source of carbon, breaking the ring structure and fully mineralizing the compound to carbon dioxide (CO$_2$) and water (H$_2$O) (Chaudry and Ali, 1988; Ramanand and others, 1988). By the adding of carbon-14 (¹⁴C) ring-labeled carbofuran to microcosms containing environmental water samples, degradation can be evaluated by examining the production of ¹⁴C-carbofuran-7-phenol and the evolution of ¹⁴C-CO$_2$.

**MATERIALS AND METHODS**

Microcosms were contained in 500-mL jars with 30-mL beakers suspended just below the inner lid by means of a wire. The 30-mL beaker held 1 mL of 0.5 N (normal) solution of sodium hydroxide (NaOH) to trap CO$_2$. Holes in the lid were covered by a Teflon-lined septum to allow for aseptic sampling of the contents of the airtight jar. The jars initially contained 50,000 counts per minute of ¹⁴C ring-labeled carbofuran (specific activity 43.2 μCi/mmol) and analytical-grade carbofuran to a concentration of 2.5 ppb. Carbofuran and ¹⁴C-carbofuran were aseptically delivered dissolved in acetone to the bottom of the dried, sterilized jars. The jars remained open for 1 hour to allow the acetone to evaporate. Aqueous field samples were mixed 50/50 with a nitrogen-free, phosphate-buffered, mineral salts medium (NFMS) (MgSO$_4$ • 7H$_2$O, 0.2 g; K$_2$HPO$_4$, 6.68 g; KH$_2$PO$_4$, 22.10 g; FeSO$_4$ • 7H$_2$O, 0.001 g; CaSO$_4$, 0.04 g; distilled water to 1 L) (Ramanand and others, 1988), and the pH of each culture was adjusted to 6.75. Soil samples to be used in the microcosms were first diluted by adding 5 g of soil to 50 mL of NFMS and stirred overnight. The pH of the soil culture also was adjusted to 6.75 before beginning the experiment. An *Achromobacter* species isolate with known carbofuran hydrolyzing activity (Karns and others, 1986; Derbyshire and others, 1987; Tomasek and Karns, 1989) was used as a positive control. The *Achromobacter* inoculum was added to a NFMS supplemented with glucose and succinate (glucose, 1 g; sodium succinate, 0.8 g; added to 200 mL of NFMS) added as carbon sources. All microcosm jars were incubated at 28 °C on an orbital shaker for the duration of the experiment.

At periodic intervals, 1-mL aliquots of the aqueous culture were removed from the jars, extracted, and analyzed using thin layer chromatography (TLC) (fig. 2). The aliquots were acidified to pH less than 1 and extracted with 1-mL aliquots of ethyl acetate. Extractions consisted of 30 seconds on a vortex mixer followed by 15 minutes in a sonicator bath. The organic layer then was pipetted off and the extraction repeated a second time. The resulting 2 mL of ethyl acetate extract then was slowly evaporated to about 50 μL using a stream of purified air. TLC was used to separate ¹⁴C-carbofuran from its metabolites. Each 50 μL of concentrated sample was spotted 1.5 cm apart and 2 cm from the bottom edge of an activated silica gel 60 TLC plate (20 × 20 cm × 0.25 mm). After the spots dried, the plate was developed using a 1:1 hexane-diethyl ether mixture. Resolution for the compounds was high with approximate retardation factors of R$_f$ = 0.25 and R$_f$ = 0.50 for carbofuran and carbofuran-7-phenol, respectively.
Separated compounds were nondestructively quantified directly from the TLC plate using a radioisotope detector. The developed plate was first wrapped in a single layer of 1.5-μm Mylar film. The TLC plates then were counted for approximately 1,000 minutes using a 1.6 × 3.2 × 0.25-mm-resolution plate. The digitally imaged TLC plates were quantified after subtracting background counts. NaOH periodically was removed aseptically from the suspended beaker in the microcosm jar, and 14C counts were determined by a scintillation counter.

RESULTS

The microcosm experiments were done with three different aqueous cultures. The first culture was a soil sample collected from an organic farm in Yolo County, Calif. (Yolo). The farm soil had no known history of exposure to carbofuran. The second culture was from an aqueous sample taken from the Colusa Basin Drain (CBD), a major agricultural drain servicing a large rice-growing area. These waters had been exposed to carbofuran, and it is these waters that will be evaluated by the methods developed in this project as part of a larger study. The third culture tested was a pure culture of the carbofuran hydrolyzing *Achromobacter* species. The *Achromobacter* species served as a positive control for the detection of carbofuran-7-phenol. Also included in the experiment was a sterile control for the CBD sample. The control was identical to the CBD culture, except that it had been sterilized by autoclaving. The sterile CBD sample represented the amount of carbofuran-7-phenol evolved through abiotic hydrolysis.

In the *Achromobacter* species microcosm experiment, greater than 80 percent of the total counts recovered from the TLC plate were in the form of 14C-carbofuran-7-phenol after 12 days (fig. 3). The percentage of
radio-labeled carbofuran-7-phenol produced by this culture continued to increase to 100 percent by 36 days. In contrast, the amount of carbofuran-7-phenol detected in the CBD microcosm was not significantly different from the sterile controls (95-percent confidence interval (n=2)). This indicates that microbial degradation was not responsible for the small production of carbofuran-7-phenol in the CBD culture. This also demonstrates the importance of having a sterile control for each microcosm treatment. The Yolo microcosm was inoculated after 27 days with cultures taken from the Achromobacter microcosm. Nine days later, microbial degradation was indicated by the detection of 74 percent of total \(^{14}\text{C}\) counts recovered as \(^{14}\text{C}\)-carbofuran-7-phenol in the Yolo microcosm. The rapid hydrolysis of carbofuran in the Yolo microcosm after adding the Achromobacter organisms indicated that microcosm conditions were suitable for microbial activity and the carbofuran was bioavailable. Therefore, the absence of microbial degradation products probably was due to a lack of carbofuran degrading organisms in the Yolo soil. Overall percentage recoveries were obtained by comparing the \(^{14}\text{C}\) counts in 1 mL of culture counted immediately on a scintillation counter to the \(^{14}\text{C}\) counts recorded after extraction and analysis of the TLC plate. The average recovery/extraction efficiencies for all samples shown in figure 3 was 66.8 percent ±6.3 percent at 95-percent confidence interval (n=24).

**CONCLUSIONS**

The microcosm method can estimate the microbial degradation of carbofuran from various field samples. The analytical procedures described allow for the processing of up to 12 samples (20 x 20 cm x 0.25 mm TLC plate) simultaneously. During the experiments the sodium hydroxide base traps were sampled and \(^{14}\text{C}\) counts were determined as an estimate of ring-cleavage carbofuran. The results indicated a problem with the experimental method, perhaps because of an increase in the volatility of carbofuran-7-phenol. Further study is needed to determine the presence and importance of carbofuran-degrading microorganisms in the agricultural drains and waterways of the Sacramento River. Additional research also could determine the effects of environmental conditions, such as dissolved organic carbon and nitrogen concentration, on these degrading populations.

**REFERENCES**

California Department of Pesticide Regulation, 1990, Pesticide use data: Computer tapes available from California Department of Pesticide Regulation, Sacramento, CA 95814.


Distributions of Organochlorine Compounds in Sediments and Livers of Striped Bass (*Morone Saxatilis*) in San Francisco Bay-Delta Estuary

*By Wilfred E. Pereira¹, Frances D. Hostettler¹, John R. Cashman² and Richard S. Nishioka³*

Abstract

A preliminary assessment was made in 1992 of chlorinated organic compounds in sediments and in livers of striped bass from the San Francisco Bay-Delta Estuary. Samples of sediment and striped bass livers contain DOT (ethane, 1,1,1-trichloro-2,2-bis(p-chlorophenyl)-) and its degradation products, DDD (ethane, 1,1-dichloro-2,2-bis(p-chlorophenyl)-) and DDE (ethylene, 1,1-dichloro-2,2-bis(p-chlorophenyl)); polychlorinated biphenyls (PCB's); alpha and gamma chlordane, and cis and trans nonachlor. In addition, livers of striped bass contained small concentrations of DCPA (dimethyl tetrachloroterephthalate), a pre-emergent herbicide. The major source of DDT in the bay probably is from runoff from the San Joaquin and Sacramento Rivers. A point source of DDT near Richmond also may be responsible for the high concentrations of DDT in the Central Bay. Ratios of pentachloro to hexachloro isomers of PCB's suggest that sources of PCB's to the South, Central, and North Bays differ. Concentrations of alpha chlordane in livers of striped bass were greater than those of gamma chlordane suggesting a greater environmental stability and persistence of alpha chlordane. Trans nonachlor, a minor component of technical chlordane, was present in greater concentrations than alpha and gamma chlordane and cis nonachlor. Trans nonachlor is more resistant to metabolism than alpha and gamma chlordane and cis nonachlor, and serves as an environmentally stable marker compound. Chlorinated organic compounds are bioaccumulated in livers of striped bass. These compounds may contribute to the decline of striped bass in San Francisco Bay-Delta Estuary.

INTRODUCTION

San Francisco Bay Estuary is the largest estuary in the Western United States. It is located at the mouth of the Sacramento and San Joaquin Rivers and drains about 40 percent of the State of California. The estuary is affected by urban, industrial, and agricultural activities. Agricultural practices in the Central Valley of California have resulted in non-point source contamination of the estuary by several first-generation organochlorine pesticides. These compounds are transported from farmlands by the Sacramento and San Joaquin Rivers into San Francisco Bay. For example, the Colusa Basin drain which discharges to the Sacramento River at Knights Landing, conveys runoff and agricultural return-flows from about 1 million acres of farmland. Chlorinated organic compounds, including DDT, chlordane, Dacthal, nonachlor, and PCB's, have been reported in fish and sediments from the Colusa Basin Drain (Turek, 1990). Many of these lipophilic organic compounds are associated with the suspended particulate load of the Sacramento and San Joaquin Rivers. These compounds are eventually dispersed throughout the estuary by tides and prevailing winds.

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to become incorporated into estuarine sediments and
accumulated in the lipophilic tissue of biota. In
addition, several chlorinated organic compounds such
as polychlorinated biphenyls (PCB's) and DDT from
point sources located on the shore of the bay have also
contributed to estuarine contamination.

Striped bass (*Morone saxatilis*) were first
introduced into the San Francisco Bay Estuary from
Chesapeake Bay in 1879. These bass supported a
commercial fishery until the 1930's. After the
commercial fishery was terminated, the estuary was
able to support a large striped bass population for
recreational fishing. However, the striped bass
population in the estuary has declined significantly
since the mid-1970's (Arthur and others, 1991). Some
of the causes for the decline in the striped bass
population include (1) reduction in egg production,
(2) loss of larval fish into water diversion projects, (3)
food limitations in the striped bass food chain, and (4)
toxic effects of pollutants (Whipple and others, 1983).

Striped bass adults are anadromous and migrate
in spring from the Pacific Ocean and San Francisco
Bay to their spawning grounds in the lower San
Joaquin and Sacramento Rivers. Spawning occurs
primarily in May. Each year hundreds to thousands of
dead striped bass are observed in the Sacramento-San
Joaquin estuary and Carquinez Strait (Kohlhorst,
1975). It has been suggested that liver dysfunction
may be an important aspect of the pathology of fish in
this die-off (Brown and others, 1987; Young and
reported that striped bass collected from the Delta
contained hydrocarbons, chlorinated hydrocarbons
and heavy metals. Recently it has been shown that the
livers of moribund striped bass were greatly
contaminated by organic chemical compounds
compared to the livers of healthy fish caught in the
Delta and the Pacific Ocean (Cashman and others,
1992). Organochlorine insecticides may cause high
mortality in fish eggs and fry with drastic effects on
survival (Holden, 1975; D. Ostrach, University of
California, Davis, CA, oral commun. 1992), but the
effects of organochlorine compounds on striped bass
and fry are not well understood.

Because the hepato-biliary tract is the primary
site of bioaccumulation and metabolism of organic
contaminants and the potential site of chlorinated
organic compounds, livers of striped bass were
selected as the target organs for this study. This report
describes some results of a preliminary assessment of

**MATERIALS AND METHODS**

**Site description**

Sample collection sites for bed sediments and
striped bass are shown in figure 1 and table 1. In
January 1992, bed sediment was collected from 17
different sites in North (San Pablo), Central, and South
San Francisco Bay. Mature striped bass were captured
in mid-May 1992, from the Sacramento River at
Knights Landing and from the San Joaquin River.

![Figure 1. Location map showing sampling sites for bottom sediments and striped bass (Morone saxatilis) in San Francisco Bay-Delta Estuary.](image-url)
Table 1. Sampling sites for bottom sediments in San Francisco Bay

<table>
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<tr>
<th>Site Number (See Fig. 1)</th>
<th>Site Name</th>
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<tbody>
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<tr>
<td>26</td>
<td>Mouth of Redwood Creek</td>
</tr>
<tr>
<td>27</td>
<td>East end, South side, San Mateo Bridge</td>
</tr>
<tr>
<td>28</td>
<td>Oyster Point entrance</td>
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<td>29</td>
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<td>Berkeley Marina</td>
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<td>Richmond Long Wharf</td>
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<td>35</td>
<td>Rat Rock, China Camp</td>
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<td>36</td>
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<td>37</td>
<td>Petaluma, Rev. #12</td>
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<tr>
<td>38</td>
<td>Sonoma Creek Mouth</td>
</tr>
<tr>
<td>39</td>
<td>East of Petaluma, #4</td>
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<tr>
<td>40</td>
<td>Richardson Bay (Shallow)</td>
</tr>
<tr>
<td>41</td>
<td>Mid-channel, East of San Bruno Shoal</td>
</tr>
</tbody>
</table>

The fish were procured by personnel from the Department of Fish and Game for purposes of spawning (in captivity) so that viable fry could be raised and used to repopulate the rivers and lakes of California.

Sample collection and analysis

Bed sediments

Samples of surficial bed sediment were collected with a Van Veen grab sampler. The upper 7 cm of sediment were sampled using a stainless steel coring barrel. The sample was stored in a clean glass jar and refrigerated. Samples were air dried and analyzed by procedures described earlier (Hostettler and others, 1989). The aromatic fraction containing the PCB’s, DDT, and chlordane was analyzed by gas chromatography-mass spectrometry (GC-MS).

Striped Bass

In mid-May, five male and two female fish were captured by electrofishing. The fish were used for spawning at the Central Valley Hatchery of the California Department of Fish and Game. In addition, five fish which were reared at the Bodega Marine Laboratories, served as controls. Control fish were offspring of adults from the delta and were raised in captivity. The fish were dissected, and livers, blood and other tissue were rapidly removed and frozen. The livers were analyzed by a previously described procedure (Cashman and others, 1992). Extracts were chromatographed on a florisil column. A hexane-ethylacetate fraction containing the compounds of interest was analyzed by GC-MS.

Gas chromatography-mass spectrometry

All samples were analyzed on a Finnigan Mat Magnum gas chromatography-ion trap mass spectrometer system, using a 30m long DB5-MS capillary column. The linear temperature program was started at 60 °C and increased to 30 °C at a rate of 6 °C per minute. All compounds were confirmed by comparing their mass spectra and retention indices with authentic standard compounds.

RESULTS AND DISCUSSION

Chlorinated organic compounds in sediments

DDT and its degradation products.

DDT was first introduced as an insecticide about 1945. Because of its toxicity, it was banned in 1972. It is estimated that approximately 1900 kg (or 2 metric tons) of DDT and its degradation products entered San Francisco Bay in 1967 from the drainage waters of the principal agricultural areas of California (Risebrough and others, 1968; Bailey and Hannum, 1967). DDT, PCB’s, and chlordane residues were reported in sediments from 26 streams tributary to San Francisco Bay (Law and Goerlitz, 1974). Low concentrations of DDT and metabolites (1-6 ng per gram) were reported in sediments of San Francisco Bay by the National Status and Trends Program of the National Oceanic and Atmospheric Administration (NOAA) (1987). A former DDT-processing plant also was located near Richmond, and it represents a point-source of DDT within San Francisco Bay.

Distributions of total DDT (DDT+DDD+DDE) in sediments of San Francisco Bay are shown in figure 2 and table 2. Concentrations ranged from 1.4 to 9 ng/g of sediments. The source of DDT in the North Bay probably is from run-off from the Sacramento and San Joaquin Rivers. The San Joaquin River has among the highest bed sediment concentrations...
concentrations of DDT, DDE, and DDD of major rivers in the United States (Gilliom and Clifton, 1990). The high concentrations of DDT near Richmond and across the bay at Larkspur Channel may be derived from the point source of DDT near Richmond. High concentrations of DDT in sediments are also found near Oakland. A sediment sample collected in the South Bay near the mouth of Coyote Creek contained the greatest concentration of DDT. Coyote Creek receives effluents from the San Jose/Santa Clara Water Pollution Control Plant.

**Polychlorinated Biphenyls (PCB's).**

PCB's were used worldwide as dielectric fluids in capacitors and in other industrial applications. It is estimated that of $5 \times 10^5$ metric tons of PCB's produced in the United States during 1930-70, approximately $3 \times 10^5$ metric tons, or 78 percent has been lost to the environment (Nisbet and Sarofin, 1972). The National Status and Trends Program of NOAA (1987) found that concentrations of PCB's in sediments collected from 4 locations within San Francisco Bay ranged from 9 to 61 ng/g. Unpublished data of the United States Environmental Protection Agency (USEPA) (Phillips and Spies, 1988) from 10 sites in South Bay sediments indicate concentrations of PCB's in the range of from below detection limits to 34 ng/g. Schmidt and others (1971) report that one of the major sources of PCB's to California Coastal waters are urban sewage outfalls. They estimated that the City of Richmond Water Pollution Control Plant, the East Bay Municipal Utility District (EBMUD), and the City of San Francisco Southeast Sewage Treatment Plant discharged about 2.6 kg/d of PCB's, or about 1 metric ton per year into San Francisco Bay (Schmidt and others, 1971).

Concentrations of PCB's in sediments collected from the 17 sites in San Francisco Bay are shown in figure 3 and table 2. Concentrations ranged from 1.3 to 8.1 ng/g total PCB's (sum of tetra, penta and hexachlorobiphenyl isomers). These concentrations are of the same order of magnitude as concentrations of DDT and its degradation products. The ratio of the pentachloro to hexachloro isomers was examined to determine source inputs of PCB's. This ratio ranged from 0.4 to 1.0 in the South Bay sediments, and from 1.1 to 4.3 in the Central and North Bay sediments. The ratios suggest different sources of PCB's to the South Bay and to the Central and North Bay sediments.

**Figure 2.** Concentrations of total DDT (DDT + DDE + DDD) in bottom sediments in San Francisco Bay, 1992.

**Figure 3.** Concentrations of total PCB's (tetra + penta + hexachlorobiphenyl isomers) in bottom sediments in San Francisco Bay, 1992.
Table 2. Concentrations of chlorinated organic contaminants in bottom sediments from San Francisco Bay in 1992
[All values in nanograms per gram dry weight]

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Chlordane

Technical chlordane is used as a pesticide in residential and agricultural areas. It is estimated that more than $6.3 \times 10^4$ metric tons of chlordane have been produced since 1946 (Dearth and Hites, 1991). About 20 to 50 percent of all the technical chlordane ever produced still exists unaltered in the environment. In 1988, the sale and use of technical chlordane were suspended. Technical chlordane contains a mixture of more than 140 compounds. The major components of technical chlordane are alpha and gamma chlordane and cis and trans nonachlor.

A high incidence (92 percent of the samples) of chlordane residues in sediments of tributaries to San Francisco Bay has been reported (Law and Goerlitz, 1974). Trace levels of cis and trans chlordane and of trans nonachlor in sediments from Islais Creek, on the eastern side of the San Francisco peninsula, were reported (Chapman and others, 1986). Distributions of total chlordane (gamma chlordane+alpha chlordane+trans nonachlor + cis nonachlor) in this study of sediments in San Francisco Bay are shown in table 2 and figure 4. Chlordane residues are present mainly in the South Bay. These chlordane residues probably originate from domestic use of chlordane as a termiticide and insecticide. The highest concentration of chlordane was found in the sediment from the vicinity of the mouth of Coyote Creek which receives effluents from the San Jose/Santa Clara Water Pollution Control Plant.

Chlorinated organic compounds in livers of striped bass

DDT and its degradation products

DDT and its degradation products have been found in bluegills and common carp from the San Joaquin River and tributaries (Saiki and Schmitt, 1986). In carp, the concentrations of total DDT approached the highest levels reported by the National Pesticide Monitoring Program for fish from other intensively farmed watersheds of the United States from 1980-1981. Total DDT in striped bass have been reported since the early 1980's (Crosby and others, 1986). Concentrations of DDT, DDD and DDE in livers of striped bass and control striped bass are shown in table 3. Ultratrace levels of DDT and its degradation products were found in some of the control samples, possibly due to transfer of DDT from female fish to offspring via the egg-yolk lipid (see Materials and Methods) (Burdick and others, 1964). In addition, samples 9 and 10 (female striped bass) contained lower levels of DDT than samples 4, 5, 6, 7 and 8 (male striped bass). In general, concentrations of DDT compounds were in the order DDE>DDD>DDT.

Chlordane

Chlordane residues have been reported in bluegills and common carp from the San Joaquin River and tributaries (Saiki and Schmitt, 1986), and in striped bass (Whipple and others, 1983). Concentrations of chlordane in livers of striped bass and control samples from this study are shown in table 2. In general, concentrations of chlordane are smaller in livers of female striped bass (sample 9 and 10) than in livers of male striped bass (samples 4, 5, 6 and 7). Chlordane was not detected in any of the control samples. Concentrations of alpha (cis) chlordane were greater than those of gamma (trans) chlordane in livers of striped bass (table 2). Alpha chlordane is environmentally more stable and hence more persistent than gamma chlordane, and thus dominates gamma chlordane in environmental samples.
Table 3. Concentrations of chlorinated organic contaminants in livers of striped bass (*Morone saxatilis*) in 1992
[All values in nanograms per gram wet weight]

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The ratio of alpha chlordane to gamma chlordane is about 0.7 to 1.0 in technical chlordane. However, the ratio is about 1.2 to 1.7 in striped bass livers again indicating the overall environmental stability of the alpha isomer. The major components in technical chlordane include gamma chlordane (24 percent), alpha chlordane (19 percent), and trans nonachlor (7 percent). In striped bass livers, the concentration of trans nonachlor is greater than alpha and gamma chlordane. Therefore, trans nonachlor is probably more resistant to metabolism than alpha and gamma chlordane. The resistance of trans nonachlor over alpha and gamma chlordane to metabolism in human tissues extracts has been reported (Sovocool and Lewis, 1975).

Polychlorinated Biphenyls (PCB's)

Stevens (1980) reported concentrations of PCB's in striped bass from the Delta for the period 1964-1976. Crosby and others (1986) postulated that concentrations of PCB's in striped bass might be sufficient to account for reproductive problems, including the resorption of eggs.

Concentrations of PCB's in the livers of striped bass and control samples are shown in table 3. PCB's were not detected in any of the control samples. Total concentrations of PCB's in livers of female striped bass (sample 9 and 10) were generally lower than samples 4, 5, 7, and 8 (male striped bass).

DCPA (Dacthal, dimethyltetrachloroterephthalate).

DCPA is a pre-emergent herbicide that is widely used in the San Joaquin and Sacramento River Basins on crops such as onions, cabbage and cotton. DCPA has been found in bluegills and common carp from the San Joaquin River and its tributaries (Saiki and Schmitt, 1986). Concentrations of DCPA in livers of striped bass are shown in table 3. DCPA was identified in six out of seven striped bass samples analyzed. DCPA was not detected in control fish.

CONCLUSIONS

Bottom sediment from San Francisco Bay and striped bass (Morone saxatilis) from the Sacramento and San Joaquin Rivers are contaminated with organochlorine compounds derived from agricultural and industrial sources. Although many of these compounds are banned from use, they continue to persist in the estuary and bioaccumulate in the livers of striped bass. These chlorinated organic compounds may be responsible in part for the hepatotoxic effects observed and may be contributing to the continuing decline of the striped bass population in San Francisco Bay. Striped bass appear to be useful bioindicators of contamination by organochlorine compounds in San Francisco Bay-Delta Estuary.

ACKNOWLEDGMENTS

We acknowledge the financial Support of the California Department of Fish and Game (Agreement FG1381) administered by the Striped Bass Stamp Committee. This work is a result of research funded in part by a grant from the National Sea Grant College Program, National Oceanic and Atmospheric Administration, U.S. Department of Commerce, under grant number NA89AA-D-SG138, project number R/F-145, through the California Sea Grant College, and in part by the California State Resources Agency. The authors wish to thank the crew of the RV Polaris for assistance with sampling of bottom sediments.

REFERENCES


A Survey of Molecular Marker Compounds in Sediments of San Francisco Bay, California

By Frances D. Hostettler¹, John B. Rapp¹, Wilfred E. Pereira¹, and Keith A. Kvenvolden¹

Abstract

An areal survey of surficial sediments in San Francisco Bay has been conducted to evaluate the presence of extractable organic compounds. Molecular marker compounds studied include hydrocarbons (PAH's), chlorinated pesticides, and other organic compounds that provide information on sources of organic input into the Bay. Fairly uniform source profiles are seen throughout the Bay. Biomarker profiles contain mature constituents indicating anthropogenic influences and extensive sediment reworking. The dominant input signatures in San Francisco Bay sediment are those of anthropogenic PAH's from combustion and other sources, and long chain \( n \)-alkanes and \( n \)-aldehydes from terrigenous vascular plants. A comparison of the sums of the combustion PAH's and the terrigenous \( n \)-alkanes shows that an anthropogenic influence is dominant in the most urban parts of the Bay close to shore, and in mid-Bay channel areas, and a terrigenous signature is dominant nearshore in San Pablo Bay and at the southernmost station in South Bay.

INTRODUCTION

San Francisco Bay is one of the world's largest urbanized estuarine systems. Its water and sediment receive organic input from a wide variety of sources. These sources include land, street, and river run-off; industrial, agricultural, and sewage discharges; atmospheric deposition; shipping traffic; and other anthropogenic inputs (Nichols and others, 1986), as well as autochthonous marine material such as algae, phytoplankton, and zooplankton. Some of the large array of organic chemicals introduced from these sources are toxic and, therefore, need to be identified and their accumulations monitored. Identifying the sources of input, both toxic and nontoxic, is a helpful step in assessing toxic accumulations as well as providing insight into estuarine sediment dynamics (Hostettler and others, 1989).

This present study is part of an on-going investigation of sources of organic constituents in surficial sediments in San Francisco Bay. Surficial sediments were collected from 17 sites throughout southern, northern (San Pablo), and central San Francisco Bay, along with one gravity core from Richardson Bay, an embayment within the Central Bay (fig. 1). These sediments were analyzed for several categories of organic compounds in order to evaluate distributions, concentrations, and possible source signatures (that is, a compound or group of compounds common to one source that identifies that source). The use of specific organic compounds to determine likely sources of organic matter in sediments is well established (Volkman and others, 1993; Brassell and Eglinton, 1986). The classes of compounds investigated in this study include hydrocarbons (\( n \)-alkanes, branched and cyclic alkanes and alkenes, biomarkers (molecular fossils), polycyclic aromatic hydrocarbons (PAH's), DDT and related pesticides, and \( n \)-aldehydes. These compounds are collectively referred to as molecular marker compounds.

¹U.S. Geological Survey, Menlo Park, CA.
Figure 1. Map of study area, San Francisco Bay.
EXPERIMENTAL METHODS

Sample Collection

Grab samples of surficial sediments were collected in January, 1992 with a Van Veen sampler from 17 sites throughout the Bay (fig. 1) at water depths of 2 to 13 m. Sediment from the top 7 cm were used for analysis. A gravity core, 112 cm deep, collected from Richardson Bay in November, 1991, was cut into vertical increments 8 cm thick, and seven representative horizons were analyzed. All samples were refrigerated immediately after collection, then transported back to the laboratory where they were frozen until analysis.

Extraction and Fractionation

Analysis focused on the unbound lipid constituents of the sediments. Sediment subsamples (100 g, air-dried, ground to pass a 32-mesh sieve) were extracted three times with a total of 400 mL of dichloromethane on a wrist-action shaker, and were centrifuged and filtered after each extraction. Each total extract was evaporated to about 5 mL, the sulfur was removed by filtering through HCl-activated copper, and the solvent was exchanged for hexane and the extract fractionated by liquid chromatography on a silica gel and alumina column. Four fractions were collected: a hexane fraction containing aliphatic hydrocarbons and biomarkers; a 20 percent benzene in hexane fraction containing aromatic hydrocarbons, PAH's, and chlorinated pesticides; a benzene fraction containing mainly n-aldehydes; and a methanol fraction containing more polar molecules. The first three fractions were examined by gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS). A method blank was carried through the entire procedure and found not to contain any of the analytes of interest.

Gas Chromatography and Mass Spectrometry

Procedures for GC and GC/MS have been described previously (Hostettler and others, 1989). In addition, the PAH's and chlorinated pesticides were quantitated on an ion-trap mass spectrometer. The gas chromatograph was maintained at 50°C. for 4 minutes, and programmed at 6 °/min to 300°C. The injector temperature was 280 °C. The capillary column (30m, 0.25 μm i.d., containing a 0.25 μm bonded phase DB-5) was interfaced directly to the ion source of the mass spectrometer.

RESULTS AND DISCUSSION

The amount of extractable organic matter (EOM) from each sample is shown in table 1. It ranged from 30 μg/gm at Pinole Point (SF-36) to 391 μg/gm at Coyote Creek mouth (SF-25). The EOM from SF-36 was anomalously low; the average value for all the other samples was 245 μg/gm. Three fractions were examined in order to identify the major constituents and evaluate possible source signatures. The constituents of this extracted matter are discussed below according to the chromatographic fractions into which they were separated.

Hexane Fraction

Gas Chromatography.--The hexane fractions show fairly uniform profiles of aliphatic hydrocarbons throughout the Bay. A typical chromatogram is given in fig. 2a. Two dominant features are obvious at all sites. The first is the n-alkane distribution. The n-alkanes range from C13 to C38 or higher. However, members C25-C31, with a strong odd-over-even carbon number predominance (OEP), are the most prominent. These n-alkanes are known to originate from the epicuticular waxes of higher (vascular) plants (Eglinton and Hamilton, 1967) and are, therefore, a signature for terrigenous input. All of the sites in this study show an n-alkane maximum at C29. Differences in maxima of these odd-carbon-number alkanes have been noted in other geochemical studies to be related to changes in watershed forest-types (Meyers and Eadie, 1993). Thus the observed uniformity of C29 predominance may indicate either a dominant local terrigenous plant source or that the majority of higher plants contributing to this signal have the same n-alkane maximum. However, a second terrigenous signal, the n-aldehydes, found in the benzene extracts and discussed below, shows promise of being somewhat more discriminative with respect to particular plant sources.

The second dominant feature of the chromatograms is the Unresolved Complex Mixture (UCM)--the chromatographically undifferentiable "hump" that underlies most of the chromatogram. A UCM indicates old petrogenic input and (or) evidence of biodegradation. Its magnitude, which is rather difficult to quantitate, in this setting gives some indication of anthropogenic contamination. Samples from all sites have a similar large UCM, except for the sample from Pinole Point, SF-36, which has essentially no UCM.
<table>
<thead>
<tr>
<th>Site</th>
<th>Location</th>
<th>Water Depth (meters)</th>
<th>EOM[^a] (μg/g)</th>
<th>OEP[^b]</th>
<th>Pr[^c]/Ph[^c]</th>
<th>Ph[^c]/18</th>
<th>ΣTERP[^d]</th>
<th>m/z 121[^e]</th>
<th>m/z 217[^e]</th>
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<td>Surface Sediments:</td>
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<td></td>
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<td></td>
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<tr>
<td>SF-25</td>
<td>Coyote Creek mouth</td>
<td>3</td>
<td>391</td>
<td>4.5</td>
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<td>2718</td>
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<td>SF-26</td>
<td>Redwood Creek mouth</td>
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<td>255</td>
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<td>0.56</td>
</tr>
<tr>
<td>SF-27</td>
<td>San Mateo Bridge, SE</td>
<td>2</td>
<td>132</td>
<td>7.8</td>
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<td>1.3</td>
<td>906</td>
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<tr>
<td>SF-28</td>
<td>Oyster Point Entrance</td>
<td>3</td>
<td>292</td>
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<td>2.5</td>
<td>1197</td>
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<td>0.57</td>
</tr>
<tr>
<td>SF-29</td>
<td>Army Street pier</td>
<td>13</td>
<td>261</td>
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<td>2.3</td>
<td>1110</td>
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<tr>
<td>SF-30</td>
<td>Alameda shoreline</td>
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<td>179</td>
<td>4.0</td>
<td>0.7</td>
<td>2.5</td>
<td>1019</td>
<td>1.2</td>
<td>0.57</td>
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<tr>
<td>SF-31</td>
<td>Oakland Outer Harbor</td>
<td>4</td>
<td>232</td>
<td>4.0</td>
<td>0.7</td>
<td>2.5</td>
<td>887</td>
<td>1.2</td>
<td>0.57</td>
</tr>
<tr>
<td>SF-32</td>
<td>Berkeley Marina</td>
<td>3</td>
<td>183</td>
<td>8.8</td>
<td>0.7</td>
<td>2.8</td>
<td>887</td>
<td>1.2</td>
<td>0.57</td>
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<tr>
<td>SF-33</td>
<td>Richmond Longwharf</td>
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<td>332</td>
<td>8.0</td>
<td>0.6</td>
<td>1.5</td>
<td>1338</td>
<td>1.3</td>
<td>0.55</td>
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<tr>
<td>SF-34</td>
<td>Larkspur Channel</td>
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<td>232</td>
<td>9.9</td>
<td>0.8</td>
<td>1.9</td>
<td>1517</td>
<td>1.3</td>
<td>0.54</td>
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<tr>
<td>SF-35</td>
<td>Rat Rock, China Camp</td>
<td>2</td>
<td>297</td>
<td>6.2</td>
<td>0.8</td>
<td>1.6</td>
<td>1812</td>
<td>1.3</td>
<td>0.57</td>
</tr>
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<td>30</td>
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<td>0.9</td>
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<td>Petaluma</td>
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<td>233</td>
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<td>1789</td>
<td>1.2</td>
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<td>Sonoma Creek mouth</td>
<td>2</td>
<td>209</td>
<td>4.3</td>
<td>0.7[^*]</td>
<td>2.0</td>
<td>1841</td>
<td>1.3</td>
<td>0.56</td>
</tr>
<tr>
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<td>Petaluma, East</td>
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<td>5.5</td>
<td>0.8</td>
<td>1.2</td>
<td>1527</td>
<td>1.3</td>
<td>0.56</td>
</tr>
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<td>SF-40</td>
<td>Richardson Bay, shallow</td>
<td>4</td>
<td>202</td>
<td>5.5</td>
<td>0.4[^*]</td>
<td>2.6</td>
<td>1104</td>
<td>1.5</td>
<td>0.54</td>
</tr>
<tr>
<td>SF-41</td>
<td>San Bruno Shoal, mid-channel</td>
<td>10</td>
<td>247</td>
<td>12.1</td>
<td>0.7[^*]</td>
<td>1.2</td>
<td>1536</td>
<td>1.3</td>
<td>0.52</td>
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<tr>
<td>SF-42</td>
<td>Richardson Bay, 0-8cm</td>
<td>190</td>
<td>10.1</td>
<td>0.8</td>
<td>2.9</td>
<td>1184</td>
<td>1.4</td>
<td>0.56</td>
<td>0.41</td>
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<tr>
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<td>&quot;</td>
<td>8-16cm</td>
<td>227</td>
<td>6.1</td>
<td>0.6</td>
<td>3.7</td>
<td>1377</td>
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<tr>
<td>SF-44</td>
<td>&quot;</td>
<td>32-40cm</td>
<td>262</td>
<td>2.4</td>
<td>0.6</td>
<td>4.4</td>
<td>1561</td>
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<tr>
<td>SF-45</td>
<td>&quot;</td>
<td>56-64cm</td>
<td>259</td>
<td>5.9</td>
<td>0.6</td>
<td>4.6</td>
<td>1347</td>
<td>1.4</td>
<td>0.56</td>
</tr>
<tr>
<td>SF-46</td>
<td>&quot;</td>
<td>88-96cm</td>
<td>298</td>
<td>4.8</td>
<td>0.6</td>
<td>2.9</td>
<td>1722</td>
<td>1.2</td>
<td>0.55</td>
</tr>
<tr>
<td>SF-47</td>
<td>&quot;</td>
<td>96-104cm</td>
<td>247</td>
<td>5.7</td>
<td>0.6</td>
<td>2.7</td>
<td>1194</td>
<td>1.3</td>
<td>0.56</td>
</tr>
<tr>
<td>SF-48</td>
<td>&quot;</td>
<td>104-112cm</td>
<td>256</td>
<td>6.1</td>
<td>0.6</td>
<td>2.4</td>
<td>1121</td>
<td>1.3</td>
<td>0.56</td>
</tr>
</tbody>
</table>

[^a] EOM = Extractable organic matter (μg/g dry weight)
[^b] OEP[^b] = \( \frac{C_{27}+6C_{28}+C_{31}}{4C_{28}+4C_{30}} \)
[^c] Pr = Pristane; Ph = Phytane; 18 = n-C_{18}. * indicates significant interference from br20
[^d] Sum of n-alkanes C_{25},27,29,31 (ng/g dry weight)
[^e] Biomarker ratios defined in text
Other features of the gas chromatograms that are present include lower range \( n \)-alkanes and the isoprenoids pristane and phytane. With only two exceptions (site 30, Alameda shoreline and site 36) the amounts of these hydrocarbons are very low relative to the terrigenous \( n \)-alkanes. Sources of these compounds might be petroleum contamination or, more likely, microbial or algal detritus, which is known to contribute \( \text{C}_{15}, \text{C}_{17} \), and pristane. The relatively low amounts present are not necessarily an indication of the magnitude of that source's contribution, however. Planktonic hydrocarbons have been found to be remineralized preferentially to other bulk organic matter within the water column (Meyers and Eadie, 1993) or during or soon after deposition in surface sediments (Prah and Carpenter, 1984).

Ratios of pristane to phytane have been used to evaluate the oxic/anoxic character of the depositional environment, but there are significant restrictions on the interpretations; values close to 1 are considered difficult to interpret (ten Haven and others, 1987; Powell, 1988). In this sample set, the values at many sites can only be estimated because of the interference of 2,6,10-trimethyl-7-(3-methylbutyl)-dodecane (referred to as \( \text{br}20 \) in fig. 2), another indicator of algal input (Cranwell and others, 1987). This interference is particularly prevalent in the South Bay. The pristane/phytane ratio values seem to be close to or slightly lower than 1 throughout this sample set. This result is consistent with values commonly observed in marine sediments (Powell, 1988). The one site where the pristane/phytane distribution is unique is site 30; this has an over-whelming abundance of pristane. This pristane abundance most likely is a result of the biota in the water column and (or) the sediment. The sediment from this site contains copious amounts of shell debris from oysters. A major source of pristane is formation in the digestive tract of copepods from phytol, the alcohol side chain of chlorophyll \( \alpha \) (Meyers and Eadie, 1993; oysters may filter-feed on these zooplankton or their debris. Thus, the pristane probably derives from this feeding cycle. In addition, the extract from this site contained uniquely high levels of phytol and sterols, also indicative of this type of recent biogenic input.

**GC/MS: Biomarkers.**—Triterpane/hopane and sterane constituents of sediments, although relatively minor components, can provide much useful information. These biomarkers, or "molecular fossils", are derived from biogenic precursors. Hopanoids are considered to originate from bacteria and blue-green algae; the relative proportions of the various hopane and hopene isomers and their progressive diagenetic counterparts are widely used as maturity and source indicators. So also are steranes related to sterols, which are derived from higher plants and animals as well as from planktonic algae (Brassell and Eglinton, 1986). The biomarkers are quantified by monitoring \( m/z \) 191 (hopanes) and 217 (steranes) ions using GC/MS Selected Ion Monitoring (SIM). Three traditional maturity indicators from the biomarker chromatograms are considered: \( \alpha\beta\text{C}_{31} \) hopane \( S/(S+R) \), which has a full maturity value of 0.6 (Mackenzie, 1984); the ratio of trisnorhopanes, \( \text{Tm/Ts} \), which here might have maturity or source implications (Seifert and Moldowan, 1978); and \( \alpha\alpha\alpha\text{C}_{29} \) sterane \( S/(S+R) \), which has a full maturity value of 0.5 (Mackenzie and others, 1980).

In this sample set the distributions of both hopanes and steranes are very uniform throughout the Bay (see fig. 2b and 2c for typical mass chromatograms and table 1 for measured biomarker parameters). With one exception (site 36, east of Pinole Point), the hopane and sterane profiles show very mature constituents. The dominant hopanes all have the \( 17\alpha\text{(H)},21\beta\text{(H)} \) (that is, \( \alpha\beta \)) configuration, as opposed to a \( \beta\alpha \) configuration present in the immature biological precursors, and the \( \alpha\beta \text{C}_{31} S/(S+R) \) ratio is very close to its full maturity value. The \( \text{Tm/Ts} \) ratios are all tightly clustered. The sterane profile shows significant maturity in that diasteranes dominate steranes, and the \( \alpha\alpha\alpha\text{C}_{29} S/(S+R) \) ratio is close to maturity. Because this degree of maturity is not likely to be a characteristic of surficial estuarine sediment, these biomarkers are probably derived from old petrogenic sources and reflect highly reworked or mixed sediments. The core in this study shows high maturity in the hopane profile, slightly lower maturity in the sterane profile, and no significant change downcore. It appears, therefore, that even to a depth of about 1 meter the sediment in this area is well-mixed and (or) heavily bioturbated, a condition typical of much of San Francisco Bay sediment (Nichols and Thompson, 1985). The slightly lower maturity of the steranes is perhaps attributable to small amounts of biogenic admixture. In general, the mature biomarker profile indicates an anthropogenic overprint on naturally lower levels of immature autochthonous biogenic input. It is interesting that at the one anomalous site, SF-36, the relative amount of extractable organic matter is very low, and the hopane/sterane profile is significantly less mature. The three maturity parameters are significantly lower than at all the other sites. The hopane profile contains high proportions of the hopene diolpentene and the \( \text{C}_{27}, \text{C}_{29}, \text{C}_{30} \), and \( \text{C}_{31}\beta\beta \)-hopanes, all of which are derived from recent biogenic input. This profile is identical.
Figure 2. Gas chromatography (GC) and GC/mass spectrometry (GC/MS) of the hexane fraction of a typical San Francisco Bay site. (a) Numbers represent carbon numbers of n-alkanes, br=branched, Pr=pristane, Ph=phytane, (b) GC/MS Selected Ion Monitoring (SIM) of m/z 191; Key shown. (c) GC/MS of m/z 217; Key shown.
to that observed at depths significantly lower than the depth interval for the above-mentioned core in a study currently in progress. Either site 36 has somehow not been subjected to the anthropogenic accumulations common to most of the rest of the Bay or has recently been scoured by dredging.

### 20 Percent Benzene Fraction

This fraction contains mostly PAH's; several of these compounds are considered highly toxic. The PAH suite in this sample set (fig. 3 and table 2) is dominated by pyrene, fluoranthene, and phenanthrene throughout the Bay. Possible sources of these compounds include combustion of fossil fuels (that is, of pyrogenic origin, deposited primarily through aeolian transport), street run-off, and petroleum (from sources such as spills, harbor traffic, and run-off from terrigenous contamination). Combustion and street run-off give very similar distributions of PAH's; this distribution is reported in many similar environments throughout the world (Laflamme and Hites, 1978). These sources can be distinguished from petrogenic input in that the former have a higher abundance of 4- and 5-ring PAH's relative to 2- and 3-ring PAH's and contain mostly non-alkylated PAH's. In contrast, the petrogenic distribution has higher levels of alkylated PAH's (for example, a ratio of methylated phenanthrene isomers to the parent PAH, MP/P, is in the range of 0-1 for combustion or pyrogenic sources and from 2-6 for petrogenic sources (Prahl and Carpenter, 1984)). It is very likely that the PAH suite in the Bay sediments contain contributions from several sources, but the dominant signature is that of combustion products/street run-off. With only one exception (at the anomalous site 36), the MP/P ratio is significantly less than 1. This PAH distribution can be considered to indicate anthropogenic input. The combustion PAH's are also the dominant signature in the total extract at many of the sites.

The relationship $\Sigma$combustion PAH/ $\Sigma$terrigenous alkanes ($\Sigma$COMB/$\Sigma$TERR; Prahl and Carpenter, 1984) gives an indication of whether an anthropogenic or terrigenous signature dominates at a given site. Similar ratios have been used previously (Hostettler and others, 1989) to show trends in input signatures. Figure 4 and table 2 show that the highest levels of PAH input are in the central urbanized part of the Bay. The sediments of the North Bay, which is less heavily urbanized, contain lower levels of allochthonous input in general; of that, there is more terrigenous input relative to anthropogenic input. Lower overall levels of input are also evident in mid-Bay or channel stations, but that may reflect the more sandy nature of these sediments. Organic constituents associate more with finer-grained particles, that is, with mud more than sand.

Many other organic constituents are also detected in this fraction, although at generally much lower concentrations than the PAH's. Chlorinated hydrocarbons such as DDT and its derivatives, other chlorinated pesticides, and PCB's are found at low concentrations at all the sites and in the core. Analysis of these compounds is reported as part of another study in this volume (Pereira and others, 1996).

### 100 Percent Benzene Fraction

This fraction was found to contain primarily a suite of long chain $n$-alkanes (see fig. 3). As with the $n$-alkanes, the high molecular weight $n$-alkanes, $C_{22}-C_{32}$, which have a strong EOP (even-over-odd carbon number preference), are known to be derived from terrigenous vascular plants (Rieley and others, 1991). However, unlike the $n$-alkanes which show a single maximum at $C_{29}$, the $n$-alkanes seem to have at least three separate groupings of homologs. These groupings are $C_{22,24}$ and $C_{26,28,30}$, both of which have a strong EOP, and a low molecular weight group, approximately $C_{12-C_{18}}$, which has no odd or even predominance but progressively higher concentrations to $C_{18}$. This latter group is probably not derived from vascular plants, but because it is in highest relative concentration at SF-30 where there are input sources from Bay organisms, it could come from a microbial, algal, or animal source. As for the first two groups, they vary in dominance around the Bay. This distribution could reflect changes in specific land-plant input, unlike the $n$-alkane distribution which shows no differentiation throughout the Bay. In a preliminary examination, when leaves from two types of trees common to the Bay area, eucalyptus and oak, were subjected to the same type of analysis, the eucalyptus leaves were found to have $C_{26,28}$ and the oak to have $C_{28,30}$ as the dominant aldehydes. This preliminary study indicates that an expanded look at aldehydes in other Bay area plant species could be useful in differentiating specific kinds of vascular plant input to Bay sediments. The fact that the aldehydes are preserved so well in the sediments when they are known to deteriorate rapidly in oxic environments implies that they are protected through the deposition stage, unlike the low-range alkanes but similar to the refractory high-range $n$-alkanes, and then preserved in the probably anoxic sediments.
Figure 3. Gas chromatograms of benzene fractions from a typical site. (a) Fraction 20B, polycyclic aromatic hydrocarbon (PAH) peaks labeled: N=naphthalene, P=phenanthrene (M=methyl derivatives), and C=Combustion PAH, from left to right: fluoranthene, pyrene, benz(a)anthracene, chrysene, benzofluoranthenes, benz(e) and benz(a)pyrene, indeno(c,d)pyrene and benzo(ghi)perylene. (b) 100B fraction, long chain n-aldehydes, carbon numbers indicated. Eucalyptus and oak leave extracts also shown.
Table 2. Concentrations of polycyclic aromatic hydrocarbons (PAH's) in surficial sediments from San Francisco Bay, in nanograms/gram dry weight

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<th>#27</th>
<th>#28</th>
<th>#29</th>
<th>#30</th>
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* Sum of "combustion" PAH. See Prahl and Carpenter, 1984; total is the same except this omits benz[e]pyrene
** Methyl phenanthrene ratio. See Prahl and Carpenter, 1984
Figure 4. Proportions of terrigenous and anthropogenic signals at study sites in San Francisco Bay.
CONCLUSIONS

This areal study of sediments throughout north, central, and south San Francisco Bay provides a baseline for future work on contaminants and sources of organic input into the Bay. In general, fairly uniform source profiles were observed throughout the Bay. Unique source profiles were observed at only two sites: the first at SF-30 where input from local marine organisms gave a high maximum for pristane, and the second at SF-36 where immature biogenic input was prominent. At all the other sites, however, including the core, biomarker profiles are dominated by mature constituents that probably were derived from old petrogenic input, indicating anthropogenic influence and highly reworked or mixed sediment.

This study showed that two source signatures dominate in the sediments: a terrigenous signal from vascular plants of high molecular weight OEP n-alkanes and EOF n-aldehydes, and an anthropogenic signal from PAH's from combustion and (or) street run-off sources. The terrigenous signal is dominant at the southernmost site in South Bay and in North Bay, closer to shore, and the anthropogenic signature is dominant in the highly urbanized areas and in the mid-Bay channel areas.

REFERENCES


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Distributions and Benthic Flux of Dissolved Sulfides in the Toxic Water Column of San Francisco Bay, California

by James S. Kuwabara1, Yvonne R. Hunter1, and Cecily C.Y. Chang1

Abstract

Chemical speciation affects the bioavailability of metals and organic ligands to planktonic and benthic organisms, as well as the partitioning of these solutes between phases. Our previous work in San Francisco Bay indicated that sulfide complexation with metals can be of particular importance because of the thermodynamic stability of these complexes. Although the water column of the Bay is consistently well-oxygenated and typically unstratified with respect to dissolved oxygen, the kinetics of sulfide oxidation could exert at least transient controls on metal speciation. Our initial data on dissolved sulfides in the main channel of both the northern and southern components of the Bay consistently indicate submicromolar concentrations (from <1 to 162 nanomolar) as one would expect in an oxidizing environment. However, chemical-speciation calculations over the range of observed sulfide concentrations indicate that these trace concentrations in the Bay water column can markedly affect chemical speciation of ecologically significant trace metals, such as cadmium, copper and zinc. In contrast to longitudinal concentration gradients for dissolved organic carbon, dissolved sulfide concentrations were typically elevated at depth suggesting a primary benthic source. Subsequent flux core and in-situ flux chamber experiments support this hypothesis.

INTRODUCTION

Trace contaminants enter major estuaries such as San Francisco Bay from a variety of point and nonpoint sources and can then be repartitioned between solid and aqueous phases or altered in chemical speciation. Recent toxicological data have consistently demonstrated that chemical speciation of trace contaminants can significantly affect the availability of those contaminants to aquatic organisms (Gavis and others, 1981; Anderson and others, 1978; Kuwabara and others, 1986). In previous studies of the South San Francisco Bay water column, two potentially important mechanisms for controls on trace-metal speciation were noted (Kuwabara and others, 1989). First, a strong correlation between two dissolved trace metals (copper and zinc) and dissolved organic substances was observed. Chemical speciation calculations were used to examine the importance of metal-organic complexation reactions. Secondly, on the basis of measurements of sulfide in the oxic water column of the ocean (Cutter and Krahforst, 1988; Luther and Tsamakis, 1989), we concluded that sulfide reactions in the water column should be considered as a controlling mechanism for trace-metal speciation in estuarine waters. Previous water-column studies in the Bay had indicated dissolved-oxygen (DO) concentrations near saturation (Smith and Herndon, 1980). One might reasonably question why sulfides could be an important factor in this oxidizing environment. However, the thermodynamic data for metal-inorganic ligand complexes (Hogfeldt, 1983; Dyrssen and Wedborg, 1989) indicated that submicromolar levels of dissolved sulfides could impose a pronounced effect on metal speciation. Therefore, the purpose of this paper is to: (1) describe the distribution of dissolved-sulfide concentrations in the northern, central and southern components of San...
Francisco Bay, and (2) because initial water column measurements indicated a benthic source for dissolved sulfides, to present subsequent benthic flux measurements for dissolved sulfides and dissolved organic carbon.

**MATERIALS AND METHODS**

Two aspects of this study involved the collection of water column and benthic flux core samples. Water-column samples were collected from the main channel of the northern, central and southern components of San Francisco Bay (fig. 1). The North Bay was sampled during a high discharge event that occurred during the spring 1991 when 173.0 to 471.1 m$^3$/s flowed from the Bay delta during March 12-15. The water-column samples were collected at three U.S. Geological Survey (USGS)- designated stations (stations 4, 8, and 18 with depths of 14, 15, and 32 m, respectively; see fig. 1). Station numbers increase in the North Bay toward the Golden Gate Bridge. The overall sampling period occurred during a multiyear drought. During the drought, the average delta outflow was 185.6 m$^3$/s between October 1, 1990 and May 31, 1991, the normally wet season. During the predrought conditions of October 1, 1984 - May 31, 1985, the average delta outflow was 440.1 m$^3$/s. We sampled the South Bay during neap

![Figure 1. Study site showing water column and benthic flux core sampling stations, San Francisco Bay, California.](image-url)
tides before, during, and after the spring phytoplankton bloom of April 1991 at USGS-designated stations 27, 32, and 36 (fig. 1). Station numbers increase in the South Bay with distance from the Golden Gate Bridge. Because of tidal variations, depths at each station varied with sampling date (table 1). At each station, samples were collected from the Research Vessel Polaris, by means of 10-L fluoroethylene polymer (FEP)-lined sampling bottles designed for trace metal sampling at three depths: 1 m from the surface, at approximately 50 percent of maximum depth, and 2 m from the bottom (hereafter designated shallow, mid-depth, and deep samples, respectively). The exception to this procedural scheme was made at the shallowest sampling station 36, where no mid-depth sample was collected.

Benthic flux experiments were made in the spring of 1992 and involved measurements from flux core and in-situ flux chambers at two sites in the South Bay: a shoal station 46 and a channel station 29A (fig. 1). This phase of the study was done in collaboration with macronutrient flux work being done by J.M. Caffrey of the U.S. Geological Survey, Menlo Park, and D.E. Hammond and W.M. Berelson at the University of Southern California. Methods for flux-core sampling have been previously described (Kemp and others, 1990). One modification that should be noted is that our samples were collected only before and after the flux-core incubation period because of sample volume constraints. Therefore, the flux determinations assume a linear change in solute concentration over the incubation period.

Dissolved sulfide concentrations were measured on site by square-wave voltammetry (Kuwabara and Luther, 1993), which involved the deposition of sulfide species at a hanging mercury electrode (-0.40 V) followed by a cathodic scan to -1.0 V to strip and detect the sulfide species. By the method of addition, only total dissolved sulfide analysis was done, as opposed to sulfide-speciation measurements, to (1) avoid sample contamination at low anticipated sulfide concentrations, and (2) complete the replicate sample analyses within 2 hours of sampling. Samples also were collected for measurement of pH and concentrations of DO (by colorimetry and the membrane electrode method), and dissolved organic carbon (by the ultraviolet/oxygen/persulfate oxidation method). Depth profiles for salinity (in Practical Salinity Units (PSU)) and temperature were obtained using a data-acquisition system with an arrangement of multiple probes to monitor various water-quality properties. Barometric pressure was determined on site for DO-concentration corrections and verified against measurements made at San Francisco International Airport (National Weather Service, oral communication, 1991).

RESULTS AND DISCUSSION

Water-Column Distributions

On the basis of temperature, salinity, and barometric pressure corrections, more than 80 percent of the DO measurements were within 90 to 110 percent of saturation, indicating that the water column at our sampling sites was an oxic environment (table 1) in which the presence of "free" sulfides (H₂S, HS⁻) was not thermodynamically favored. Measured pH values were fairly uniform throughout the sampling period, with more than 60 percent of the values were 7.9 to 8.0 (table 1).

In the North Bay, the dissolved organic carbon (DOC) concentrations increased significantly in the direction of freshwater sources and generally decreased with depth (table 1). In the South Bay, the DOC concentrations also increased with distance from the mouth of the estuary. However, the horizontal DOC gradient was not as pronounced as it was in the North Bay (table 1), and, as with salinity, no vertical DOC gradient was observed in the South Bay, which received little freshwater input.

In contrast to DOC distributions, no discernable longitudinal gradient was noted for dissolved sulfides in the North or South Bay (table 1). Relative to concentrations of surface samples, the sulfide concentrations were elevated (although < 1 μM) at depth. A significant (at the α=0.05 level) positive correlation between relative depth and measured sulfide concentration indicated a benthic source of sulfide (Kuwabara and Luther, 1993).

Benthic Fluxes

Sulfide benthic fluxes were consistently positive (out of the sediment) over the course of our sampling period in 1992 (table 2). This was consistent with our hypothesis of a primary benthic source, based on initial concentration distributions in the water column. Flux experiments during spring 1993 (a post-drought
period) examine the possibility of a water-column-sulfide source resulting from the spring phytoplankton bloom.

In contrast to sulfide fluxes, DOC fluxes changed direction over the period of study, going from negative to positive (table 2). Trace metal flux measurements will provide information on the association of the trace metals with the benthic exchange of sulfide and dissolved-organic ligands.

Kuwabara and Luther (1993) used chemical-speciation calculations to demonstrate the potential importance of dissolved sulfides as ligands in the oxic San Francisco Bay water column. Their analysis indicated that, as the dissolved sulfide concentration declined below the dissolved copper concentration (30 nanomolar), copper complexation with humic material, with stability constants that are lower than stability constants associated with copper sulfide

Table 1. Water-column data for the northern and southern components of San Francisco Bay, California.

[Dissolved oxygen (DO) is given as percent saturation; salinity (SAL) in practical salinity units (PSU); water-column temperature (TEMP) in degrees Centigrade; dissolved organic carbon concentration (DOC) in milligrams carbon per liter and dissolved sulfide concentration in nanomolar. Symbol "*" indicates that the measurement was not made.]

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complexes, became increasingly important. Hence, the concentration of uncomplexed, and presumably more bioavailable, copper increased. This range of calculated copper ion activity is ecologically relevant because it brackets toxic copper concentrations for phytoplankton groups (for example, negative log of the copper concentration (pCu) of 8.5 to 10.9 for diatom species; Gavis and others, 1981). The competition between DOC and dissolved-sulfide complexation for control of trace-metal speciation was evident when dissolved-sulfide concentrations were above 5 percent of the dissolved copper concentrations. Similar to copper, an analogous sulfide effect on cadmium and zinc speciation over observed concentration ranges for these trace metals was also reported although the dominant, nonsulfide species for cadmium and zinc differed (Kuwabara and Luther, 1993). Given the observed dissolved-sulfide-concentration range in these oxic waters, there is clearly a potential for ecologically significant effects on trace-metal speciation.

Table 2. Benthic fluxes with 95 percent confidence intervals using n=3 analytical replicates per sampling interval of dissolved organic carbon and sulfides in South San Francisco Bay.

[Dissolved organic carbon (DOC) flux in millimoles per square meter per hour; and sulfide flux in micromoles per square meter per hour. Paired flux measurements indicate determinations made on replicate cores.]

<table>
<thead>
<tr>
<th>Sampling Date</th>
<th>DOC Flux</th>
<th>Sulfide Flux</th>
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<tr>
<td>Shoal Station 46</td>
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<td>March 17, 1992</td>
<td>-0.94±0.43</td>
<td>0.14±0.03</td>
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<td>April 13, 1992</td>
<td>-0.80±0.33</td>
<td>.16±0.03</td>
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<tr>
<td>May 11, 1992</td>
<td>.08±0.11</td>
<td>.37±0.09</td>
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<td>1.92±0.15</td>
<td>.42±0.09</td>
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<tr>
<td>1.45±0.08</td>
<td>0.42±0.03</td>
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<tr>
<td>Channel Station 29A</td>
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<tr>
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<td>-.83±0.17</td>
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<td>.55±0.10</td>
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REFERENCES


Luther, G. W., and Tsamakis, E., 1989, Concentration and form of dissolved sulfate in the oxic water column of the ocean: Marine Chemistry, v. 27, no. 3-4, p. 165-177.

Past and Present Research on Metal Transport In St. Kevin Gulch, Colorado

By Briant A. Kimball

Abstract

To prepare for mitigation of the effects of acidic mine drainage on upland watersheds, process-oriented research at St. Kevin Gulch has focused on chemical reactions that affect metal transport and partitioning among phases. We operationally defined dissolved and colloidal transport phases and the speciation of iron because the cycle of iron can affect the cycling of other metals. With these phases defined, our approach was to study chemical reactions in the context of hydrologic transport. By establishing the hydrologic setting with tracer-dilution injections, we studied temporal and spatial variability in metal concentrations resulting from combined hydrologic and chemical processes. Temporal and spatial aspects of variation were combined in an instream pH-modification experiment to evaluate the kinetics of reactions involving metals. These data are the focus of a simulation model that combines transport and reactive chemistry of metals. Ongoing studies of the ecological system are in anticipation of higher pH and lower metal concentrations that should follow remediation by a passive treatment system.

INTRODUCTION

Many streams in upland watersheds are affected by acidic mine drainage (Moore and Luoma, 1990). Efforts are underway to mitigate the effects of this acidic drainage. However, successful mitigation requires an understanding of the processes that affect metals in these streams. Since 1986, the Toxic Substances Hydrology Program of the U.S. Geological Survey has supported field-based research on processes that affect metals in streams. Objectives of this research include: (1) The study of instream chemical and biological processes in the context of transport processes that affect them, (2) determination of the role of sediment and colloids in the processes affecting metals, (3) quantification of the temporal and spatial variability of processes, and (4) simulation of the reactive transport of metals to evaluate field observations. The purpose of this report is to present the major findings from past studies of St. Kevin Gulch and to describe the focus of present studies.

St. Kevin Gulch is an upland watershed in the Rocky Mountains; its elevation is 2,500 to 2,800 m (meters) above sea level and it has an area of about 10$^2$ km (square kilometers, fig. 1). Most annual precipitation falls as snow; snowmelt runoff that occurs in late May or early June is the dominant hydrologic event each year. Bedrock is a quartz-biotite-feldspar schist. Mining of silver and zinc sulfides in vein deposits mostly occurred around 1920. St. Kevin Gulch has been a valuable research site because of its combination of physical and chemical characteristics: (1) Metal concentrations are sufficiently high to be quantified by routine methods and yet not so high as to be serious health and safety concerns, (2) a 100-m reach is a point source of acidic inflow, (3) physical and chemical processes that affect metal concentrations occur downstream from the principal acidic inflows, (4) a single algal species, *Ulothrix* sp., predominates (McKnight, 1985), and (5) a natural wetland is present just upstream from the confluence of St. Kevin Gulch and Tennessee Creek (fig. 1).

Downstream changes in the chemical characteristics and discharge in St. Kevin Gulch result from acidic inflows (fig. 2). Upstream from the principal
EXPLANATION

Sample site with distance in meters from lithium chloride injection site

**EXPLANATION**

Sample site with distance in meters from lithium chloride injection site

![Diagram showing location of injection site and subsequent points along St. Kevin Gulch.](image)

**Figure 1.** Location of (a) St. Kevin Gulch, near Leadville, Colorado, and (b) location of pH-modification experiment in 1988

acidic inflows (0-363 m, fig. 1) the chemical composition mostly results from natural weathering in the basin. Between 363 m and 501 m, discharge of the acidic inflows is only about 0.8 L/s (liters per second) compared to 6 L/s in the stream, but the inflow chemistry strongly affects instream pH and metal concentrations (figs. 2a and 2b). The confluence with the nonacidic Shingle Mill Gulch is a short distance downstream from the acidic inflows, at 501 m. At the confluence, discharge approximately doubles (fig. 2c) and pH increases from the nonacidic inflow. Downstream from 526 m there only are a few acidic inflows from small mines; these inflows do not substantially change instream metal concentrations upstream from the wetland. The mass loading of manganese (Mn) (fig. 2d) shows that the acidic inflows between 363 m and 501 m are virtually a point source to the stream.

**Past Studies**

We have taken advantage of the characteristics of St. Kevin Gulch to conduct process-oriented research, studying well-known chemical reactions in the context of hydrologic transport. Using tracer-dilution injections to establish the hydrologic background, we have carried out experiments with intensive spatial and temporal sampling (table 1).

**Methods for Assessing Iron-Rich Systems**

Particular methods have been used to define processes that affect metals in acidic mine drainage. We will review some of these methods and then discuss how these methods aid the study of instream processes.

*Setting the hydrologic framework.*—Use of experimentally injected chemical tracers helps to define relevant physical characteristics of a stream. With the physical characteristics defined, it is possible to distinguish between physical and chemical effects on instream metal concentrations (Stream Solute Workshop, 1990; Bencala and others, 1990; Broshears and others, 1993). However, a seasonal study has a greater temporal scale, and it is not always practical to inject tracers to set the hydrologic framework. In such cases, natural conservative solutes can substitute for...
Table 1. Summary of experiments in St. Kevin Gulch, 1986 through 1993

<table>
<thead>
<tr>
<th>Date</th>
<th>Description</th>
<th>Results</th>
</tr>
</thead>
</table>
| August 1986   | LiCl injection for 36-hour diel, synoptic sampling, and hydrologic characterization. | 1. Documentation of iron photoreduction reaction (McKnight and others, 1988).  
2. Hydrologic characterization (Broshears and others, 1993).  
| August 1987   | LiCl injection for synoptic sample for filtered and particulate concentrations.                                                    | 1. Comparison of rates for hydrologic and biogeochemical processes; evaluation of particulate concentrations (Kimball and others, 1994). |
| August 1988   | LiCl injection for diel sampling; nighttime synoptic sampling; pH-modification experiment.                                          | 1. Mechanisms of iron photoreduction reaction (Kimball and others, 1992b).  
3. Temporal and spatial data on metal response to increased pH (Kimball and others, 1992a; Kimball and others, 1994).  
| August 1990   | Hillslope interactions; injection of radioactive phosphorous for identification of nutrient pathways.                              | 1. Water exchange between stream and alluvium (Harvey and Bencala, 1993).  
2. Phosphate uptake (Tate and others, 1991). |
| 1990          |                                                                                                                                         |

injected tracers (Bencala and others, 1987). Although this procedure does not establish absolute values of discharge as does the tracer-dilution method, it accounts for the hydrologic effects by a discharge ratio so that chemical effects can be studied.

Defining transport phases.—In addition to defining the hydrologic framework, it is necessary to define transport phases for the metals. The cycle of iron (Fe) affects many metals and is strongly affected by precipitation (Kimball and others, 1991) and by photoreduction (McKnight and others, 1988; Kimball and others, 1992b). At pH values greater than about 2.2, Fe oxyhydroxides commonly precipitate to form colloids, which affect the cycling of other metals by sorption (Smith and others, 1991). Colloids in St. Kevin Gulch can contain as much as 130 ppm (parts per million) arsenic (As), 230 ppm copper (Cu), 600 ppm lead (Pb), and 1,200 ppm zinc (Zn). However, Ranville (1992) determined that most of the suspended sediments in St. Kevin Gulch are primarily aggregates of colloidal (40-nanometer diameter) Fe oxyhydroxides and Fe oxyhydroxysulfates. In opposition to precipitation, photoreduction of Fe III can dissolve colloids and return ferrous iron (Fe II) to the stream (McKnight and others, 1988). Other metals that may be sorbed to the colloidal Fe also can be released. This dynamic cycling of Fe on a daily time scale affects the transport and transformation of other metals and can be studied only by adequate sampling for Fe phases and species.

Operational definitions of phases can be defined by using multiple filtrations. The definitions that are most meaningful in terms of the Fe colloids include the following: (1) filtered concentration (representing...
"dissolved" solutes) determined by filtration through a 0.001-μm (micrometer) pore-size membrane, (2) colloidal concentration, determined by filtration through a 0.45-μm pore-size membrane and then subtracting the dissolved concentration, and (3) suspended particulate concentration determined by an unfiltered sample and then subtracting the colloidal and dissolved concentrations. These definitions are time consuming to obtain when we could not take the time for the sequence of filtrations. For intensive temporal and spatial sampling, we generally obtained only an unfiltered and a 0.1-μm filtered sample (McKnight and others, 1988; Kimball and others, 1992a).

**Instream Processes**

With these definitions of transport phases, we have described instream processes affecting metals in the context of transport.

*Photoreduction of iron*—Intensive temporal sampling showed the importance of the photoreduction process on the cycling of Fe and other metals. Quantification of discharge allowed the calculation of mass flow and flux of Fe II from the streambed to the water column in response to light intensity (see fig. 3 in Kimball and others, 1992b).

*Coupling of rates for hydrologic and chemical processes*—Intensive spatial sampling along a 1,800-m reach allowed us to compare rates of transport to rates of chemical reaction by using steady-state solute transport simulation (fig. 3). If chemical reactions are relatively fast compared to rates of transport, the reactions can affect instream concentrations. The solid line in figure 3a illustrates conservative transport of Fe. Adding first-order rate constants to simulate Fe removal indicates the relative importance of chemical reaction (dashed line, fig. 3a). The increase of colloidal Fe (fig. 3b) corresponds to the decrease of filtered Fe. Loss of colloidal Fe (dashed line simulation, fig. 3b) is from sedimentation of colloidal aggregates.

*Response to pH modification*—Combining intensive temporal and spatial sampling, we modified the chemistry of St. Kevin Gulch to document the kinetics of metal reactions as pH was increased in two steps (fig. 4a). With an increase of pH to near 6.0, aluminum (Al) was completely partitioned from the filtered to the colloidal phases in the water column (fig. 4b). This is likely from the rapid formation of an Al oxyhydroxysulfate complex (Kimball and others, 1994). Sorption onto colloids affected the concentrations of Cu. However, Mn and Zn were little affected at this level of pH (Kimball and others, 1994).

*Exchange of streamwater and subsurface water*—By injecting tracers both in the stream and in the hillslope, the exchange of water between the stream and the alluvium was documented (Harvey and Bencala, 1993). This changes the traditional concept of the stream as a pipe of water leaving a watershed. Instead, the stream continues to interact with the watershed, which can affect instream metal concentrations because metals are present in substantial concentrations in the alluvium (J.W. Harvey and B.A. Kimball, U.S. Geological Survey, 1991, unpublished data, Salt Lake Oty, Utah). The scale of this interaction can be on the order of 1-m stream segments.

*Treatment of metals by natural wetlands*—Before entering Tennessee Creek, the metal-rich water from St. Kevin Gulch passes through a natural wetland. Initial sampling of inflow and outflow water from this wetland indicated that metals were being

![Image](image-url)
treated by interaction with organic matter and minerals of the wetland. Metal flux and geochemical processes in this wetland have been studied by Walton-Day (1992) to determine whether the wetland is removing Fe, Mn, cadmium (Cd), Cu, Pb, and Zn from surface water flowing through the wetland. Careful measurement of metal fluxes indicates that only Fe was removed from surface water. Most metals were untreated by the wetland, and essentially passed through despite prolonged physical contact with the wetland environment.

**PRESENT STUDIES**

In our current work, we have used mathematical models to provide a frame of reference for evaluating data from field studies. We developed computer simulations for conservative and reactive solute transport in St. Kevin Gulch. Reactive transport simulation takes the study of biogeochemical processes beyond batch experiments and places it in the context of hydrology.

**Simulation of conservative transport**—Physical effects on the transport of solute mass must be quantified to distinguish the chemical and biological effects. Simulation of transport in mountain streams presents certain unique physical aspects, the most prominent being transient storage (Bencala and Walters, 1983). The transport model developed by Bencala and Walters (1983) was improved by using a new algorithm and by execution on new generations of computers (Runkel and Broshears, 1992; Runkel and Chapra, 1993). These improvements were the basis for building the simulation model for reactive solute transport.

**Simulation of reactive solute transport**—Data from the pH-modification experiment in 1988 (as in fig. 4) provide a unique opportunity to evaluate our understanding of rates for metal reactions. The complexity of reactive chemistry is simulated by coupling MINTEQA2 (Allison and others, 1991) with the transport code (Runkel and others, 1996; Broshears, 1996).

Our understanding of geochemical reactions in St. Kevin Gulch has provided the background to study remediation of acidic mine drainage. The State of Colorado plans to install a passive treatment system near the mine dump in St. Kevin Gulch, creating the opportunity to study the changes that occur in the recovering stream. Chemical changes in the water column, in the bed sediment, and in the alluvium will combine to affect the stream ecosystem. The current dominance of the blue-green algae, _Ulothrix sp._ (McKnight, 1988) will be affected by chemical changes, indicating the ecosystem response. Combining this remediation study with our past and present studies will complete a comprehensive process-oriented study at the St. Kevin Gulch site.

**REFERENCES CITED**


Iron and Zinc Budgets in Surface Water for a Natural Wetland Affected by Acidic Mine Drainage, St. Kevin Gulch, Lake County, Colorado

By Katherine Walton-Day

Abstract

Iron and zinc mass input and output in surface water were estimated for a wetland receiving acidic mine drainage near Leadville, Colorado, to evaluate (1) whether the wetland is removing the metals from surface water, and (2) the processes causing the observed metal fate. The results indicate that about 560 and 850 kilograms of iron were removed from surface water from late spring through fall 1988 and from late spring through midsummer 1989, respectively. Iron removal occurred primarily through settling of iron oxyhydroxide particles greater than 0.1 micrometer. The results also indicate that zinc was not removed from surface water by the wetland. All of the zinc is in the filtered fraction. Either contact time between the water and the wetland substrate is insufficient for the reactions that could remove dissolved zinc, such as sulfate reduction, to occur, or zinc removal reactions do not occur in this wetland.

INTRODUCTION

Studies of wetlands used to treat acidic mine drainage (AMD) commonly compare concentrations of metals at inflow and outflow locations to assess treatment efficiency. Wieder (1988) suggested instead that studies of wetland-treatment systems should consider the mass or mass rate of metal transported into and out of these systems. Comparison of inflow and outflow concentrations fails to include effects of hydrologic processes, such as addition of clean water by springs and evapotranspiration, which cause dilution and concentration, respectively, that are unrelated to chemical interactions between water and substrate. Both processes are important in studies of natural wetlands. In this study, a natural wetland that receives AMD was studied to (1) use stream discharge and water-quality data to estimate iron and zinc mass input and output, and any net retention of either metal in the wetland over the time intervals studied; and (2) identify hydrologic and geochemical processes causing current (1988-89) metal transport and fate of metals in the wetland.

STUDY-SITE DESCRIPTION

The wetland has an area of about 26 ha and is located about 7 km northwest of Leadville, Colo. (fig. 1). The wetland receives 99 percent of its surface water from six sources: Temple Gulch, Gleason Gulch, North Spring, St. Kevin Gulch, South Spring, and Porcupine Gulch Ditch (which flows intermittently) (fig. 1). The weathering of pyrite in the mineral deposits in St. Kevin Gulch produces AMD. A principal source of AMD (pH = 2.7, iron and zinc concentrations > 100 mg/L) emanates from mine-waste piles located about 2 km upstream from the discharge of St. Kevin Gulch into the wetland. The AMD is diluted by the water in St. Kevin Gulch to a pH of 3.5 to 4.5, and to iron and zinc concentrations of up to 10 mg/L. Previous work in the wetland indicates that most metal loading occurs during spring runoff (May through July). During this period, flow from St. Kevin Gulch comprises from 50 to 85 percent of the flow into the wetland. In addition, discharge from St. Kevin Gulch into the wetland is intermittent and ceases during low-flow periods.

Hydrologic budgets for the two time periods of interest were previously constructed (Walton-Day, 1991), and the results are listed in table 1. The budgets balanced within 4 percent in 1988 and about 10 percent in 1989; therefore, the budgets account for all major components of flow into and out of the wetland.
Figure 1. Location of wetland showing flume, streamflow gage, and sampling sites. Location of the channel for Porcupine Gulch is approximate.

Table 1. Hydrologic budget for St. Kevin wetland

<table>
<thead>
<tr>
<th></th>
<th>Surface water</th>
<th>Ground water</th>
<th>Precipitation</th>
<th>Storage</th>
<th>Total</th>
</tr>
</thead>
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<tr>
<td>1988 inputs</td>
<td>660</td>
<td>7</td>
<td>20</td>
<td>61</td>
<td>750</td>
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<tr>
<td>1989 inputs</td>
<td>950</td>
<td>6.3</td>
<td>24</td>
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<td>980</td>
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</tbody>
</table>

Surface-water flow dominates the hydrologic budget. Most of this flow (80 percent or greater) occurred during May and June of each year. These results justify the assumption that surface water is the primary component in the element budgets presented herein. Exceptions to this assumption are described in the Results and Discussion section.

METHODS

Iron and zinc mass budgets for the wetland were constructed using surface-water discharge and water-quality data from May through October 1988, and May through July 1989. Surface-water flow into and out of the wetland was monitored by fiberglass Parshall flumes located on the five inflow streams (except
Porcupine Gulch Ditch) and by a streamflow gage at the wetland outflow (fig. 1). Stream stage was recorded at each site every 30 minutes from about May 18–November 10, 1988, and from about May 4–September 30, 1989. A combination of stage-discharge relations and rating curves developed over the measurement periods were used to calculate discharge at the sites as detailed by Walton-Day (1991). A continuous record was not obtained for Porcupine Gulch Ditch, but was developed using data from the other streams (Walton-Day, 1991). Errors in discharge measurements were estimated to equal ±10 percent (Walton-Day, 1991).

Surface-water samples were collected every 3 to 4 weeks from June 1–November 10, 1988, and every 2 weeks from May 4–July 13, 1989. Grab samples were collected in the narrow, turbulent throats of the flumes where the water was well mixed. At the streamflow gage, samples were composited from three to seven grab samples collected at various locations across the narrowest section of the stream. Two aliquots—one unfiltered and acidified (representing total recoverable metal concentrations), and the other filtered (0.1 μm membrane) and acidified (representing filterable metal concentrations)—were collected for analysis of iron and zinc concentrations. Iron (1988 and 1989 samples) and zinc (1988 samples) concentrations were determined using inductively coupled plasma-atomic emission spectrometry (Lichte and others, 1987). Zinc concentrations in 1989 samples were determined using an inductively coupled plasma-mass spectroscopy system. Combined analytical and sampling errors were estimated to be ±5 percent (Walton-Day, 1991).

Iron and zinc budgets in surface water for the two time periods were calculated as follows:

\[ R_T = \sum \text{MF}_{\text{INFLows}} - \text{MF}_{\text{OUTFLOW}}, \quad (1) \]

where

- \( R_T \) is retention through time, the net gain or loss of a constituent from the wetland in kilograms, and
- \( \text{MF} \) is the calculated load (mass flow) of the constituent at the inflows and outflow for the period of time considered.

When \( R_T \) is positive, the constituent is accumulating in the wetland. When \( R_T \) is negative, the constituent is being flushed from the wetland. When \( R_T \) is zero, or there is no significant difference between the mass of the constituent in the inflows and outflows, then the wetland has no effect on transport of the constituent.

Constituent loads were calculated using either a concentration calculated by use of the continuous discharge record or average constituent concentration; when the regression relation between the natural logarithms of measured concentrations and associated stream discharge was significant (95 percent confidence level), then the regression was used to calculate constituent concentration with the following equation:

\[ C_{\text{CALC}} = e^b \cdot Q^m, \quad (2) \]

where

- \( C_{\text{CALC}} \) is the concentration of the species (in micrograms per liter), calculated from the discharge \( Q \) (in liters per second);
- \( m \) is the slope; and
- \( b \) is the y intercept of the regression line.

The load in a stream through time is

\[ \text{MF}_{\text{STREAM}} = 8.64 \times 10^{-5} \sum_{i=1}^{n} [Q_i \cdot (e^b \cdot Q_i^m)]. \quad (3) \]

where

- \( \text{MF}_{\text{STREAM}} \) (\( = \text{MF}_{\text{INFLOW}} \) or \( \text{MF}_{\text{OUTFLOW}} \)) is the load (in kilograms) of a species of interest over the time period of interest,
- \( 8.64 \times 10^{-5} \) is a conversion factor that incorporates the number of seconds in a day and converts micrograms to kilograms, and
- \( Q_i \) is the average daily discharge of the stream over \( n \) days.

When the regression relation between concentration and discharge was not significant at the 95 percent confidence level, then average concentrations were used to calculate constituent load by the following equation:

\[ \text{MF}_{\text{STREAM}} = 8.64 \times 10^{-5} \cdot C_{\text{AVG}} \sum_{i=1}^{n} Q_i. \quad (4) \]

where

- \( \text{MF}_{\text{STREAM}} \) is the load (in kilograms) of a species over the time period of interest,
- \( C_{\text{AVG}} \) (in micrograms per liter) is the mean concentration of the species based on samples collected at the stream over the period of interest, and
- \( Q_i \) is the average daily discharge of the stream over \( n \) days.

The error in the estimates of load (where load is the product of concentration and discharge) is ±15 percent, the sum of the errors of the concentration and discharge measurements.
Table 2. Average concentrations of iron and zinc in surface water in St. Kevin Gulch and tributaries, 1988-89
[All concentrations are in micrograms per liter. Unfilt. indicates concentrations in unfiltered water samples. Filt. indicates concentrations in filtered water samples]

<table>
<thead>
<tr>
<th>Element and fraction</th>
<th>Temple Gulch</th>
<th>Porcupine Gulch Ditch</th>
<th>Glosson Gulch</th>
<th>North Spring</th>
<th>South Spring</th>
<th>St. Kevin Gulch</th>
<th>Wetland Outflow</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron (unfilt.)</td>
<td>850</td>
<td>1,200</td>
<td>160</td>
<td>410</td>
<td>350</td>
<td>670</td>
<td>430</td>
</tr>
<tr>
<td>Iron (filt.)</td>
<td>270</td>
<td>180</td>
<td>50</td>
<td>150</td>
<td>60</td>
<td>160</td>
<td>180</td>
</tr>
<tr>
<td>Zinc (unfilt.)</td>
<td>100</td>
<td>290</td>
<td>13</td>
<td>150</td>
<td>250</td>
<td>4,200</td>
<td>4,500</td>
</tr>
<tr>
<td>Zinc (filt.)</td>
<td>95</td>
<td>250</td>
<td>14</td>
<td>160</td>
<td>230</td>
<td>4,000</td>
<td>4,600</td>
</tr>
</tbody>
</table>

RESULTS AND DISCUSSION

Comparison of average values in table 2 shows that concentrations of unfiltered iron are greater than concentrations of filtered iron at almost every site, indicating that particulate iron is a major component of the total iron load entering the wetland. Unfiltered and filtered zinc concentrations do not significantly differ relative to the analytical error. In a few instances, average concentrations of zinc in filtered samples are slightly greater than in unfiltered samples. This discrepancy reflects analytical and rounding errors and is considered negligible. Consequently, only the loading estimates for unfiltered zinc are shown on table 3. Table 2 also shows that inputs to the wetland other than St. Kevin carry elevated concentrations of metals. These inputs represent minor contributions to the total load during spring runoff but are the major contributors to metal loads when flow into the wetland from St. Kevin Gulch ceases. The data in tables 2 and 3 indicate that average concentrations were used to calculate all loads except loads of unfiltered zinc in South Spring, of unfiltered iron and zinc at the St. Kevin Gulch inflow to the wetland, and of unfiltered zinc at the wetland outflow. The linear regression relations between the natural logarithms of discharge and constituent concentration are significant at the 99 percent confidence level for all relations in table 3 except for unfiltered zinc concentrations at the wetland outflow, which are significant at the 95 percent confidence level. Loads of all metals (table 4) were greater in 1989 than in 1988 despite the fact that loads were calculated over a shorter time period in 1989. The difference occurs because the continuous

Table 3. Regression relations used to calculate unfiltered iron and zinc concentration at locations where the relations between the natural logarithms of discharge and concentration were statistically significant
[Unfilt. indicates relations developed from concentrations measured in unfiltered water samples. * indicates that linear relationship between the natural logarithms of discharge and concentration was not significant, and the mean values in table 2 were used to calculate the metal load. \( C_{C_{ALC}} \) calculated concentration of the species in micrograms per liter; \( e \), base of the natural logarithm; \( b \), y-intercept of the regression line between the natural logarithms of discharge and concentration; \( Q \), average daily discharge; and \( m \), slope of the regression line between the natural logarithms of discharge and concentration. All relations significant at the 99 percent confidence level, except zinc at wetland outflow, is significant at the 95 percent confidence level]

<table>
<thead>
<tr>
<th>South spring</th>
<th>St. Kevin Gulch</th>
<th>Wetland outflow</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron (unfilt.)</td>
<td>( C_{C_{ALC}} = e^{0.81}Q^{0.32} )</td>
<td>( C_{C_{ALC}} = e^{0.81}Q^{0.32} )</td>
</tr>
<tr>
<td>Zinc (unfilt.)</td>
<td>( C_{C_{ALC}} = e^{0.84}Q^{0.76} )</td>
<td>( C_{C_{ALC}} = e^{0.82}Q^{0.19} )</td>
</tr>
</tbody>
</table>

recorders were installed earlier in 1989 than in 1988, and, therefore, a higher proportion of the spring runoff was included in the 1989 calculations than in the 1988 calculations. This difference illustrates the importance of spring runoff to the loads carried into and out of the wetland. By including 2 extra weeks of spring runoff in the 1989 calculation, loads are 20 to 80 percent greater than in 1988 even though the period after July was not included in the 1989 calculation. The data in table 4 also show that mass inflows differ significantly from outflows only for iron in both years. There is no significant difference between input and output loads of zinc for either year because the differences between input and output loads are not greater than the ±15 percent error associated with the calculations.
Table 4. Total loads in surface-water input and output of the wetland. 1988 and 1989
[Loads in kilograms. 1988 loads calculated for May through October. 1989 loads calculated for May through July. Unfilt. indicates loads are based on concentrations from unfiltered water samples. Filt. indicates loads are based on concentrations from filtered water samples. Bold type for a value in the "Net" row indicates that the value is significant. Net is significant when smaller value +15 percent is less than larger value -15 percent]

<table>
<thead>
<tr>
<th></th>
<th>1988</th>
<th></th>
<th>1989</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Iron load</td>
<td>Zinc load</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Unfilt.</td>
<td>Filt.</td>
<td>Unfilt.</td>
<td></td>
</tr>
<tr>
<td>Input</td>
<td>760</td>
<td>360</td>
<td>1,600</td>
<td></td>
</tr>
<tr>
<td>Output</td>
<td>200</td>
<td>110</td>
<td>1,500</td>
<td></td>
</tr>
<tr>
<td>Net</td>
<td>560</td>
<td>250</td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>

The difference in net retention of filterable and unfiltered iron (table 4) indicates that the settling of iron oxyhydroxide particulates in the greater than 0.1-μm iron accumulated in the wetland sediments. Net removal of filterable iron (table 4) may be caused by (1) precipitation of iron oxyhydroxides, (2) aggregation and settling of colloidal iron oxyhydroxide floc, (3) formation of iron sulfides, (4) sorption, and/or (5) organic complexation of iron. However, the relatively low permeability of the wetland substrate and short residence times of water in the wetland restrict the amount of water in contact with the wetland substrate in which processes 3-5, above, occur. Therefore, most iron removal probably occurs through physical settling of particulate iron oxyhydroxides and through aerobic processes that promote the formation of iron oxyhydroxides in the filterable size fraction. The lack of significant, current (1988-89), accumulation of zinc conflicts with recent research on wetlands that indicates zinc accumulation in wetland sediments through sulfate reduction (Machemer and Wildeman, 1992). The most likely explanations are that (1) loading rates of zinc onto the wetland are too great, and residence times too short to allow sufficient contact time between zinc and the wetland substrate where sulfate reduction occurs, and/or (2) that sulfate reduction is not occurring in this wetland.

The difference between the budget results for iron and zinc relates to the dominant forms of each metal in surface water and to the mechanisms that can remove each metal in a wetland environment. Most of the iron is present in the particulate or suspended-sediment fraction of the inflow loads and can be removed from surface water simply by settling where water velocities in the wetland decrease. This process requires no interaction between the water column and wetland substrate. Conversely, all of the zinc is present in dissolved form. The processes that could remove zinc in the wetland include sulfate reduction and precipitation of sulfide minerals, and sorption. Both of these processes require contact between the water and wetland substrate. The lack of detectable zinc removal in this wetland, at least within the range of error of the measurements, indicates that the contact time between the water and the wetland sediments is not sufficient for these processes to occur, and/or that the processes do not occur to a significant extent in this wetland. The assumption that surface water is the only component of the element budgets is valid for zinc but not for iron. Additional data in Walton-Day (1991) indicate that when ground-water transport was included in the 1988 budget, the amount of iron that appeared to be accumulating in the wetland, based on the results of the surface-water mass budget, was balanced by an equivalent amount of iron being transported downward out of the wetland sediments into the underlying aquifer. This result does not invalidate the budgets presented here, but indicates that iron dynamics in the wetland are more complicated than the simple surface-water budget suggests. Additional research is needed to understand these dynamics.

SUMMARY

Calculations of annual loads of iron and zinc in a wetland receiving drainage from St. Kevin Gulch show that loads of iron in inflow significantly and consistently exceeded loads in outflow, whereas loads of zinc in inflow and outflow did not differ significantly. The wetland sediments removed 560 and 850 kg of iron from surface water in 1988 and 1989, respectively. Settling of particulate iron oxyhydroxide material from the greater than 0.1-μm size fraction accounts for 60 to 70 percent of the iron removed from surface water during transport through the wetland. This process also may remove filterable iron. This budget only includes the surface-water components of element transport and, therefore, excludes the complex dynamics that affect iron transport in ground water in this wetland.

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The lack of detectable zinc removal probably results from inadequate residence time of water with the wetland substrate during the period of maximum loading (spring runoff); that is, the hydraulics of this natural wetland system do not allow sufficient contact time between the substrate and most of the water for the reactions to occur that can remove zinc. It is also possible that processes that can remove zinc, such as sulfate reduction, simply are not occurring at a sufficient rate to affect zinc transport in this wetland.

REFERENCES


Tracer Injections in Small Streams—Why and How We Do Them

By Gary W. Zellweger

Abstract

By using simple techniques and imagination, researchers can use conservative-tracer injections to collect hydrologic data on small streams. Stream hydrologic properties such as discharge, which cannot be measured in small streams by other means, are measurable with a precision as good as two percent by use of conservative tracers.

This paper briefly describes some of the hydrologic information that can be gained from continuous injection experiments and describes tracer selection criteria, injection equipment, and sampling and tracer analysis.

INTRODUCTION

Researchers can use tracers to learn more about stream hydrology than just an occasional measurement of discharge or time of travel. Hydrologists have successfully used tracers to collect discharge data, calculate dissolved loads, calibrate flumes, and follow the flow paths of surface water and ground water through subsurface zones, by using tracer injections that may last from a few minutes to several days, depending on the application. Calculations of hydrologic properties using tracer data range from simple equations to complex mathematical models. Because conservative tracers travel with water, tracers allow us to "label" water and observe its movement.

The purpose of this paper is to explain how hydrologic information can be collected from continuous injection of conservative tracers, chiefly anionic tracers injected into small streams, and to provide details and guides on the techniques of tracer injection. The intent is convince the reader of the value of tracer injections and encourage their use in hydrologic studies.

WHY WE DO THEM

Tracer experiments may have begun long ago when the first hydrologist stirred up the muddy bottom of a lazy stream and watched the turbidity cloud move downstream, spreading as it flowed, traveling faster through the middle of the stream and slower at the edges, gradually dispersing until it was invisible. This quaint image captures the essence of tracers. They provide the ability to observe the movement of water and measure hydrologic properties of streams and stream channels. Tracer research is not new; the historical use of tracers was reviewed by Spencer and Tudhope (1958).

A conservative tracer, by definition, does not react with streamwater or the stream channel in any manner that either increases or decreases the mass of tracer. This property allows the researcher to use conservative tracers to acquire knowledge about the hydrology of small streams.

Knowledge that can be gaine from a well-planned and executed tracer experiment includes time of travel, instantaneous discharge, temporal and longitudinal variation in discharge, dispersion, rates of ground-water inflow and stream outflow (by difference in discharge), flow in the subsurface zone, losses and gains of dissolved compounds such as heavy metals or nutrients, stream and subchannel transient storage, and mixing of surface water and groundwater. Samples of anionic tracers can be analyzed with a precision of about 1 percent, and some hydrologic properties can be calculated on the basis of concentrations of tracers with a precision as good as two percent (Zellweger, 1993).

HOW WE DO THEM

Tracer injections are composed of three parts: tracer selection, delivery, and sampling and analysis.
Tracer Selection

Among the criteria to consider when selecting tracers are measurability, solubility, availability, background concentration, cost, and conservativeness. For most applications conservativeness of the tracer is not merely important, it is crucial.

The choice of tracers is generally limited to the stable anions: chloride, bromide, and sulfate, or organic dyes. Of these, chloride as sodium chloride and sulfate as magnesium sulfate (Epsom salt), share the advantage of being inexpensive. Infrequently, sulfate may not be conservative when dissolved oxygen concentration is low, and the dissolved organic carbon concentration is great enough that bacteria might reduce sulfate.

The characteristics of several fluorescent dyes were described by Smart and Laidlaw (1977). Rhodamine WT is commonly used for water tracing; its use is described by Wilson and others (1986). However, rhodamine is not always conservative. Rhodamine fluorescence decreases rapidly in acidic, metal-rich, sunlit streams (Zellweger and others, 1987). Bencala and others (1983) found that rhodamine was lost in a pool-and-riffle, gaining stream, where a large amount of the surface water passed through streambed sediment.

In low order, pool-and-riffle streams with coarse gravel beds and low discharge, a significant portion of flow may pass over and through the sediment beds. Under these conditions dyes tend to be lost whereas anionic tracers remain conservative.

In higher order streams that are less pool-and-riffle, have greater discharge, and have a greater flow to bed-surface ratio, dye loss to sediment is less important. Under these conditions dyes perform well; anionic tracers also perform well, but the mass required, milligrams per liter for ions verses micrograms per liter for dyes, is a disadvantage.

Anions and dyes can be thought of as complementary tracers--anions for small streams and dyes for larger streams.

Delivery System

In a continuous injection tracer study, a concentrated solution of tracer is added to a stream at a steady rate. The delivery system includes a reservoir of injectate and a pump for delivering the injectate to the stream.

Sampling and analysis

Streamwater samples for measuring the concentration of conservative tracers do not need to be filtered when collected; however, the analytical method or...
instruments may require that samples be filtered when analyzed. New polyethylene bottles are not highly contaminated with tracer anions; rinsing them with sample water before filling should remove the highly soluble tracer ions. Because it is easier to collect additional samples than to interpolate between scattered data or to repeat experiments, it is advisable to collect abundant samples, including samples of background tracer concentrations.

Chloride, bromide, and sulfate concentrations can be readily measured by ion chromatography. Chloride and bromide can also be analyzed colorimetrically, however the method forms the same color with chloride as with bromide, so that the analysis is difficult to interpret if both ions are present. Both methods have a precision of about 1 percent.

**CALCULATIONS**

Simple to complex hydrologic properties can be calculated from the results of a continuous tracer injection. After a continuous injection begins the tracer concentrations at locations downstream of the injection point increase from background values, which could be zero, to the steady state or "plateau" values.

The calculation of discharge is an example of a simple calculation (Kilpatrick and Cobb, 1985) that requires the injectate concentration, injection rate, the background concentration, and a plateau concentration downstream to the injection point. More elaborate calculations, such as determining dispersion equation parameters, can be made using data collected as the concentration increases to the plateau (Bencala, 1984).

**SUMMARY**

A large amount of hydrologic information can be obtained from a continuous injection of conservative tracers by use of techniques that have been field tested and are easily learned. The methods are simple to use and are adaptable to field conditions. Supplies are inexpensive, and equipment is not difficult to use. Calculations of some hydrologic properties can be made with an accuracy as good as about 2 percent.

**REFERENCES**


Processes Controlling Dissolved Copper Concentrations during an Instream pH-Modification Experiment

By Kathleen S. Smith

Abstract

Changes in dissolved copper (Cu) concentrations as a function of pH were observed during an instream pH-modification experiment conducted in St. Kevin Gulch, Colorado, a stream affected by acidic mine drainage. Understanding the processes that control dissolved Cu concentrations is important because dissolved Cu can pose health risks and contaminate receiving waters. Comparison of dissolved Cu concentrations during the instream experiment with changes in dissolved Cu concentrations in inbottle simulation experiments performed with streamwater in the absence of streambed sediment shows good agreement. These data indicate that processes controlling Cu attenuation with increasing pH occur primarily in the water column. Sorption reactions and (or) coprecipitation reactions with iron and (or) aluminum precipitates forming in the water column in response to increasing pH may be the processes controlling Cu partitioning in these systems. Predictive computer modeling of Cu sorption onto hydrous ferric oxide slightly underestimates Cu attenuation observed in the instream system.

INTRODUCTION

St. Kevin Gulch is a small subalpine stream affected by acidic mine drainage. An instream pH-modification experiment was conducted at St. Kevin Gulch to examine the response of chemical species in this stream to pH changes (Kimball and others, 1994). The ambient pH of St. Kevin Gulch is about 3.5.

As pH increases, several reactions can take place, including precipitation, sorption, and coprecipitation reactions. In the pH range of the instream pH-modification experiment (pH about 3.5-6) several major elements, especially iron (Fe) and aluminum (Al), will likely be controlled by precipitation reactions and many trace elements will be controlled by sorption and (or) coprecipitation reactions. Reactions that appear to control Cu concentrations during the instream pH-modification experiment are examined in this paper. Smith (1991) has demonstrated that pH-dependent Cu adsorption by iron-rich sediment seems to control Cu concentrations in experiments conducted with streamwater and streambed-sediment mixtures collected from St. Kevin Gulch.

The objective of this paper is to compare information from the application of different approaches used to evaluate processes that control Cu concentrations under changing pH conditions. These approaches include inbottle simulation experiments, computer-model predictions, and field observations during an instream pH-modification experiment.

STUDY METHODS

On August 25, 1988, the instream pH of a reach of St. Kevin Gulch was increased from ambient (about pH 3.5) to about pH 6 by injecting Na₂CO₃ dissolved in streamwater at a site along the stream (fig. 1). There were two steps in the pH modification. The first pH step involved constant injection of the Na₂CO₃ solution for a 3-hour period during which time the pH increased to just above 4. The second pH step included constant injection of the Na₂CO₃ solution at an increased rate for a 3-hour period during which time the pH increased to almost 6. Water samples were continuously collected at four sites downstream from the injection point during the course of the instream pH-modification experiment.
Unfiltered and filtered (0.1μm nitrocellulose filters) water samples were collected, and pH and temperature were measured. Study site 1 (fig. 1) is 24 m from the injection point. More detailed information about the injection procedure can be found in Kimball and others (1994).

On August 24, 1988, a series of in-bottle simulation experiments were conducted to examine pH-dependent partitioning of Cu between water and sediment from St. Kevin Gulch. Composite samples of streamwater and of iron-rich streambed sediment suspended in streamwater were collected along the reach of stream used for the instream pH-modification experiment.

Dispensed into a series of polyethylene bottles was 40 mL of either the bed sediment/streamwater suspension or of streamwater with no sediment. The pH was adjusted in the bottles by addition of differing amounts of 0.1 mol/L Na₂CO₃ to obtain a pH range from ambient to pH >6. No other substances were added. The bottles were allowed to sit for approximately 6 hours at stream temperature with occasional shaking. Care was taken to shield the bottles from sunlight. After the 6-hour period, part of the contents in each bottle was separated by filtration through 0.1-μm nitrocellulose filters. The filtrates were saved for chemical analysis and final pH's were measured in the remaining portions.

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**Figure 1.** Map showing the reach of St. Kevin Gulch, Colo., used for an instream pH-modification experiment, the injection point of Na₂CO₃, and downstream sampling locations. (From Kimball and others, 1992, fig. 1.)
in the bottles. Determination of the solute concentrations remaining in solution at each pH was used to determine pH-dependent partitioning reactions. In the inbottle simulation experiments conducted with streamwater in the absence of the sediment, solute loss represents solubility reactions and (or) metal sorption (and (or) coprecipitation) onto particulates precipitated in the water column as a result of pH adjustment. Water samples were analyzed using inductively coupled argon plasma-atomic emission spectrometry (ICP-AES) and ion chromatography.

Adsorption of Cu onto hydrous ferric oxide (HFO) for conditions during the instream pH-modification experiment was modeled using the Generalized Two-Layer Sorption Model (GTLM) and data base of equilibrium surface-complexation constants of Dzombak and Morel (1990). The same HFO properties were used in these modeling exercises as were used by Dzombak and Morel to fit the surface-complexation constants. The GTLM evokes a two-site model for cation sorption that includes a subset of high-affinity cation-binding sites. It assumes that M$^{2+}$ is the only metal species that sorbs to HFO and that HFO is the sole sorbent material.

Computer-model simulations were conducted using the equilibrium speciation program MINTEQA2, version 3.00 (Allison and others, 1991). This program incorporates the GTLM and computes adsorption reactions and solution equilibria simultaneously in a self-consistent manner. St. Kevin Gulch water chemistry from site 1 (fig. 1) at one of the sampling times was input to MINTEQA2. The pH was fixed at desired values (incremental values ranging from 3.5-6). Particulate suspended-iron values were determined by subtracting the Fe concentration in filtered water from the Fe concentration in unfiltered water. In order to calculate the amount of sorbent HFO present, 15 particulate suspended-iron concentrations, which were measured during the times when the instream pH was $>5$ at site 1, were averaged (0.65 mg/L iron). It should be emphasized that all of the model input was derived either from chemical analysis of St. Kevin Gulch water or from information provided by Dzombak and Morel (1990). None of the model parameters were modified, and no fitting parameters were used in these computer simulations.

**PROCESSES THAT CONTROL COPPER CONCENTRATIONS UNDER CHANGING pH CONDITIONS**

Variation of dissolved Cu with stream pH and particulate suspended-iron concentrations at study site 1 (fig. 1) is depicted in figure 2. This figure illustrates the effect of both pH and particulate iron on dissolved Cu.

![Figure 2](image_url)

**Figure 2.** Variations in concentrations of dissolved copper and particulate suspended iron, and stream pH at study site 1 during an instream pH-modification experiment, St. Kevin Gulch, Colo.
concentrations. As the stream pH increases, the amount of particulate suspended iron increases and the dissolved Cu concentration decreases. There is a corresponding shift of part of the dissolved Cu phase to a particulate phase. This shift indicates either precipitation, coprecipitation, and/or pH-dependent sorption of the Cu. Dissolved Cu concentrations as a function of pH are shown in figure 3 for both the instream pH-modification experiment at study site 1 (fig. 1) and the inbottle simulation experiments. Dissolved Cu concentrations in the inbottle simulations conducted with streamwater in the absence of streambed sediment (hollow triangles) provide a very close match to the dissolved Cu concentrations observed during the instream pH-modification experiment (hollow circles). This indicates that most of the Cu attenuation processes are occurring in the water column rather than by interaction with bed sediment.

Smith (1991) has demonstrated that iron-rich streambed sediment can control Cu attenuation by pH-dependent adsorption reactions in laboratory simulations using natural materials from St. Kevin Gulch. In both the inbottle simulation experiments discussed in this paper and the experiments conducted by Smith (1991), St. Kevin Gulch streambed sediment was placed in direct contact with streamwater and the two materials were mixed together; As such, these experiments maximized the contact between water and sediment. Although there is abundant iron-rich streambed sediment along the reach of St. Kevin Gulch used for the instream pH-modification experiment, there is no evidence of dissolved Cu attenuation by the bed sediment (fig. 3). Possible reasons that dissolved Cu concentrations do not appear to be controlled by interaction with bed sediment may include (1) hydrologic controls that prevent equilibration of dissolved constituents in the water column with the bed sediment (especially over short distances), (2) the presence of a stagnant liquid film at the water/bed-sediment interface that retards diffusion of dissolved constituents, (3) the physical proximity of suspended sediment to dissolved constituents, and (4) differences in sorption site-binding energies between the suspended particulates and the bed sediment. In order for Cu to adsorb onto HFO surfaces, Cu ions are thought to

![Figure 3](image-url)
form an inner-sphere surface complex. To form an inner-sphere surface complex, waters of hydration between surface atoms and the Cu ion must be removed. The presence of a stagnant liquid film (possibility 2) at the water/bed-sediment interface might interfere with the formation of inner-sphere surface complexes by retarding the diffusion rate of dissolved ions and waters of hydration.

The possibility that iron-rich suspended particulates control partitioning of Cu between the dissolved and particulate phases was tested using a MINTEQA2 computer simulation. The results are illustrated in figure 4. The computer simulation predicts no adsorption between pH 3.5 and 5, which corresponds to observations from the instream pH modification experiment. However, at pH > 5.5 the computer simulation slightly underestimates Cu partitioning. This could be due to several considerations. First, the concentration of particulate iron is very small (averaging 0.65 mg/L, which corresponds to 0.001 g/L HFO, 5.8 x 10^-8 mol/L of high-energy binding sites, and 2.3 x 10^-6 mol/L of low-energy binding sites under conditions where dissolved Cu is 2.7 x 10^-6 mol/L). Surface-complexation models are not as reliable under conditions of high adsorbate/adsorbent ratios. Dzombak and Morel (1990) have tried to overcome this problem by developing a method to include the effects of surface precipitation into the GTLM. This is accomplished by adjusting the surface complexation constants by a constant factor that incorporates a solubility product for ferric hydroxide and a surface precipitation reaction for the hydroxide of the sorbing cation. Incorporation of surface precipitation effects into the GTLM was not done in the present study. Another explanation for computer model underestimation of Cu attenuation is that HFO is not the sole sorbent material. Aluminum hydroxide precipitates were observed forming during the second pH step of the pH-modification experiment (Kimball and others, 1992). It is likely that some dissolved Cu may be sorbed and (or) coprecipitated by these aluminum hydroxide precipitates.

**Figure 4.** Comparison of computer model predictions (solid curve) and observations from an instream pH-modification experiment (hollow circles) for dissolved copper as a function of pH, St. Kevin Gulch, Colo.
SUMMARY

Subtle changes in dissolved Cu concentrations were observed during an instream pH-modification experiment conducted along a reach of St. Kevin Gulch, Colorado. There is close agreement between changes in dissolved Cu concentrations as a function of pH during the instream experiment and changes in dissolved Cu concentrations in inbottle simulation experiments performed with streamwater in the absence of streambed sediment. These data indicate that processes controlling Cu attenuation with increasing pH occur primarily in the water column. Sorption reactions and (or) coprecipitation reactions with iron and (or) aluminum precipitates forming in the water column in response to increasing pH likely control Cu partitioning in these systems. Predictive computer modeling of Cu sorption onto hydrous ferric oxide slightly underestimates Cu attenuation observed in the instream system. However, concentrations of particulate suspended iron are small, which reduces reliability of the model predictions.

ACKNOWLEDGMENTS

The work described in this paper is part of a much larger effort for the Upper Arkansas River Surface-Water Toxics Project. I would like to thank Briant Kimball and Katie Walton-Day for their helpful reviews of this manuscript. Analytical support was provided by Paul Briggs, David Fey, and John McHugh.

REFERENCES

An Equilibrium-Based Simulation Model for Reactive Solute Transport in Small Streams

By Robert L. Runkel¹, Kenneth E. Bencala² and Robert E. Broshears³

Abstract

A reactive solute transport model that considers the physical and aphysical processes affecting solutes in small streams is presented. The model is developed by coupling an existing solute transport code with a model of chemical equilibria. The resultant model considers a variety of physical and chemical processes including advection, dispersion, transient storage, precipitation/dissolution, sorption/desorption and the deposition of particulate metal oxides.

INTRODUCTION

Numerous streams and rivers in the United States are adversely impacted by acid mine drainage. In addition, many streams are naturally acidic. Given acidic conditions, trace metals are more soluble and may be present in significant concentrations within the water column. This is an important phenomenon, as many trace metals are toxic to fish and other aquatic organisms. Due to the acid mine drainage problem, investigators are currently studying mountain catchments. Some of the ongoing research involves field-scale experiments to quantify the various processes affecting trace metals in streams. These experiments often involve the addition of an acid or a base to alter the rates of pH-dependent processes.

Two such experiments are those described by Broshears and others (1996) and McKnight and Bencala (1989). In the first experiment, a sodium carbonate solution was injected into Saint Kevin Gulch, a small mountain stream located near Leadville, Colorado. This injection resulted in an increase in pH that was accompanied by precipitation of iron and aluminum. In addition, copper was removed from the water column via sorption reactions. A second pH perturbation experiment was conducted on the Snake River, a naturally acidic stream located near the continental divide in north central Colorado, and involved an injection of sulfuric acid to decrease pH. This depression of pH resulted in an immediate increase in dissolved iron concentrations, due to the dissolution of hydrous iron oxides and the photoreduction of ferric iron.

Both of the experiments above involve complex processes that are difficult to quantify. Mathematical models provide a means of analyzing the processes that affect trace metals in natural systems. Solute transport models, for example, are used to study the physical processes that affect water quality. Models of chemical equilibria, meanwhile, are used to quantify chemical reactions in batch systems, wherein the effects of transport are not considered. Recently, complex ground water simulation models have been developed that couple hydrologic transport and chemical equilibrium. These models are used to quantify the nature and extent of various chemical and biological processes, in the context of hydrologic transport. Although many models are currently available for conventional contaminants, few models consider both physical transport and chemical equilibria for the case of trace metals in surface waters. In the research described herein, an equilibrium-based solute transport model for small streams is described.

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MODELING EFFORTS

Many water quality models have been developed to assess the fate and transport of conventional contaminants, such as biochemical oxygen demand (BOD) and organic nitrogen, and environmental parameters, such as dissolved oxygen and temperature. Closely related to the water quality models are the solute transport models described by several authors (Zand and others, 1976; Bencala and Walters, 1983). As opposed to modeling eutrophication-dissolved oxygen dynamics, these models are concerned with the transport of inorganic solutes including salts and trace metals. Like the water quality models, solute transport models describe the physical processes of advection and dispersion and some specific chemical and biological reactions. Simple solute transport models representing physical processes alone are useful tools for analyzing data obtained from tracer injection experiments. More complex models are developed by adding kinetic and/or equilibrium-based reactions. Examples of such nonconservative models include the work of Somlyody (1978), who described a model for heavy metals based on first-order reaction kinetics; and the research of Bencala (1983), in which a kinetic sorption model was developed for strontium.

A major shortcoming of most solute transport models is the simplistic nature in which reactive chemistry is considered. Existing models rely primarily on the specification of kinetic rate constants and on simple partition-coefficient representations of sorption phenomena. For the case of inorganic solutes, the database of kinetic rate constants is strikingly sparse, and many sorption reactions are thought to obey more complex sorption laws. While these transport models provide an accurate description of physical transport, they fail to include the degree of chemical sophistication needed to model pH perturbation experiments like those described above.

Chemical equilibrium models, in contrast, are useful in describing chemical equilibria in batch systems, but do not consider transport processes. When the chemical reactions of interest are relatively fast and reversible or the time scale of study is of sufficient length, chemical equilibria may be assumed. Models of chemical equilibria are founded on the mass-action equations that describe the equilibrium ratios of chemical species. Given the total mass of the chemical components and a set of equilibrium constants, the chemical species present at equilibrium are determined.

Fortunately, many chemical reactions are ‘sufficiently fast’ relative to hydrologic processes, such that chemical equilibrium may be assumed. Given this local equilibrium assumption (LEA) (Rubin, 1983), it is possible to negate the disadvantages of both models by using a transport model to describe physics and an equilibrium model to describe chemistry. Indeed this is the approach taken by numerous authors for solute transport in groundwater systems (for example, Cederberg and others, 1985; Engesgaard and Kipp, 1992). Surprisingly, few models using the transport/equilibrium approach exist for surface waters.

The present work is directed towards developing a general model that expands the earlier work of Chapman and others (1982), who studied a short stream reach using a model that couples a semi-analytical solution of the advection-dispersion equation with the MINEQL chemical equilibrium code (Westall and others, 1976). Several differences are of note. First, the model developed below uses a numerical solution of the transport equations, rather than the convolution integral approach employed by Chapman. In addition, the governing transport equations include a transient storage mechanism. Second, the model is applied over a much larger spatial scale. Finally, special attention is applied to the process of dissolution from stationary surfaces.

MODEL DEVELOPMENT

The general approach taken here is to couple an existing solute transport code with a chemical equilibrium model. The resultant model considers the physical processes of advection, dispersion, transient storage and the deposition of colloidal metal oxides, as well as the chemical processes of speciation, precipitation/dissolution and sorption. Consideration of these processes provides a general modeling system for the simulation of inorganic constituents in streams and rivers.

The solute transport model used for this work is developed by Runkel and Broshears (1991). This model is based on a one-dimensional advection-dispersion equation with additional terms to account for lateral inflows and transient storage. Transient storage is a useful empirical representation of a storage phenomenon that has been noted in small streams. Additional details of the transient storage approach are provided by Bencala and Walters (1983). In general,
the solute transport model may be thought of as a set of partial-differential equations describing the physical transport of multiple solutes. The chemical equilibrium model is based on MINTEQ (Allison and others, 1991), a sophisticated geochemical model. Given analytical concentrations of the chemical components, MINTEQ computes the distribution of chemical species that exist within a batch reactor at equilibrium. These equilibrium computations include the precipitation and dissolution of solid phases as well as sorption processes. The mass-action equations describing equilibria form a set of nonlinear algebraic equations.

Given a coupled set of algebraic and partial-differential equations, several solution techniques are available. A common method is known as the sequential iteration approach (Yeh and Tripathi, 1989), wherein each model time step is divided into a ‘reaction’ step and a ‘transport’ step. During the reaction step, the algebraic equations describing chemical equilibria are solved for each segment in the stream network. In doing so, the equilibrium model determines the solute mass in dissolved, precipitated and sorbed forms. Based on this information, a transport step is taken in which the partial-differential equations describing transport are solved. In this step, the mobile phases of each solute are transported downstream. Because the solution steps neglect the coupling of the transport and chemistry, the procedure iterates until a specified level of convergence is achieved.

Assumptions

Several assumptions are embodied in the development of the surface water equations that follow. The assumptions inherent to the problem are summarized as follows:

• **Chemical Equilibria.** -- Perhaps the most important assumption for the model developed here is the premise that complexation, precipitation and sorption reactions are in a state of chemical equilibrium. This assumption is based on the premise of local equilibrium, wherein chemical processes are considered sufficiently fast relative to hydrologic transport.

• **One-Dimensional Transport.** -- A second assumption is that the stream is of small to moderate width and depth, such that one-dimensional transport is applicable. Under this assumption, solute mass is assumed to be uniformly distributed over the stream’s cross-sectional area. Given one-dimensional transport, the physical processes of advection, dispersion, lateral inflow and transient storage are considered.

• **Mobile and Immobile Phases.** -- Solute mass for each chemical component is distributed among five distinct phases. The first three phases represent dissolved, precipitated and sorbed mass present in the water column. These three phases are mobile, in that they are subject to the effects of transport processes. The final two phases represent precipitated and sorbed mass that resides on the bed of the stream or is attached to stationary debris in the stream channel. As such, these final two phases are immobile and are not affected by transport mechanisms.

• **Precipitation.** -- Dissolved mass in the water column may form precipitates if the solution becomes oversaturated with respect to the defined solid phases. Any precipitated mass initially resides in the water column and is subject to transport, until settling processes cause it to become immobile or redissolution returns it to the dissolved phase. This assumption states that precipitation occurs in the water column exclusively, and precipitation directly to the immobile bed is excluded. Precipitated mass may accumulate on the bed, however, as mass is deposited via settling.

• **Dissolution.** -- When the aqueous solution is undersaturated, dissolution occurs preferentially from the water column. Under this scenario, all of the precipitate in the water column is allowed to dissolve before precipitate on the bed is subject to dissolution. This is a reasonable assumption, considering the intimate contact between precipitates in the water column and the flowing waters.

• **Transport of Precipitates and Settling.** -- Any precipitates formed in the water column are sufficiently small, so as to be transported at a velocity that is identical to that for the dissolved species. This assumption obviates the need for a more sophisticated treatment of solids, such as sediment transport modeling. Transported precipitates are subject to the force of gravity and settle at a rate defined by a settling velocity. The settling rate of a particle is unaffected by other solids in solution (that is, unhindered settling).
**Sorption/Desorption.** -- Dissolved species may sorb to solid phases present in the water column or to sorption sites present on the bed of the stream. Conversely, sorbed species may desorb from sites in the water column or on the bed.

**Governing Equations**

With these assumptions in hand, the fundamental equations governing reactive solute transport in surface waters are presented. These equations are formulated for each chemical component defined within the equilibrium model. In short, chemical components are the fundamental building-blocks from which all chemical species are derived. As defined in MINTEQ, chemical reactions involve two or more components that react to form a chemical species. In general, the components must linearly combine to form every possible species in the system, and no component may be formed as a combination of other components (Allison and others, 1991).

To begin, the total component concentration, \( T \), is defined by

\[
T = C + P_w + P_b + S_w + S_b
\]  

(1)

where \( C, P_w, P_b, S_w, \) and \( S_b \) are the total dissolved, mobile (water-borne) precipitate, immobile (bed) precipitate, mobile sorbed, and immobile sorbed concentrations. The total component concentration \( (T) \) is composed of five separate phases, as given by Equation and depicted in Figure 1, where the surface water system is represented as two separate compartments. The first compartment represents the water column wherein the three mobile phases \( (C, P_w, \) and \( S_w) \) are found. The second compartment is the immobile substrate, such as the streambed or debris, onto which water-borne precipitated and sorbed phases deposit. This compartment contains the two immobile phases, \( P_b \) and \( S_b \).

Figure 1 provides a convenient summary of the processes affecting each phase. The dissolved phase \( (C) \), for example, is affected by transport processes, as represented by the transport operator, \( L() \). In addition, the dissolved concentration is affected by precipitation/dissolution and sorption/desorption reactions within the water column (interactions with \( P_w \) and \( S_w) \). Finally, \( C \) is affected by dissolution of precipitate from the immobile substrate and by sorption/desorption from immobile sorbents (interactions with \( P_b \) and \( S_b) \). Note that the settling process affects both the precipitated and sorbed phases in the water column \( (P_w \) and \( S_w) \), as given by the settling velocities \( v_{pl} \) and \( v_{st} \) \([LT^{-1}]\), respectively.

A differential equation describing conservation of mass for the total component concentration \( (T) \) is derived by developing mass balance equations for the five phases and summing them to yield

\[
\frac{\partial T}{\partial t} = L(T) - L(S_b + P_b) + S_{ext}
\]  

(2)

where \( t \) is time, \( S_{ext} \) is a source/sink term representing external gains and losses and \( L() \) is the transport operator given by

\[
L(\tilde{C}) = -\frac{Q}{A} \frac{\partial}{\partial x} (\tilde{C}) + \frac{1}{A} \frac{\partial}{\partial x} (AD \frac{\partial}{\partial x} (\tilde{C})) + \frac{q_{LIN}}{A} (\tilde{C}_L - \tilde{C}) + \alpha (\tilde{C}_S - \tilde{C})
\]  

(3)

where

\( \tilde{C} \) - concentration of an arbitrary component phase (for example, \( T, S, \) or \( P_b) [M L^{-3}] \),

\( \tilde{C}_L \) - solute concentration in lateral inflow associated with \( \tilde{C} [M L^{-3}] \),

\( \tilde{C}_S \) - storage zone solute concentration associated with \( \tilde{C} [M L^{-3}] \),

\( A \) - stream channel cross-sectional area \([L^2]\),

\( Q \) - volumetric flowrate \([L^3 T^{-1}]\),

\( x \) - distance \([L]\),

\( D \) - dispersion coefficient \([L^2 T^{-1}]\),

\( q_{LIN} \) - lateral inflow rate \([L^3 T^{-1} L^{-1}]\), and

\( \alpha \) - storage zone exchange coefficient \([T^{-1}]\).

Inspection of Equation reveals that \( T \) is a function of \( P_b \) and \( S_b \). Equations for these phases are given by

\[
\frac{\partial P_b}{\partial t} = \frac{v_{pl}}{d_i} (P - P_b) - f_b
\]  

(4)

\[
\frac{\partial S_b}{\partial t} = \frac{v_{st}}{d_i} (S - S_b) - g_b
\]  

(5)

where

\( f_b \) - source/sink term for dissolution from the immobile substrate,

\( g_b \) - source/sink term for sorption/desorption from the immobile substrate,

\( v_{pl} \) - settling velocity for the precipitated phase \([LT^{-1}]\).
\( v_{sl} \) - settling velocity for the sorbed phase \([LT^{-1}]\),

\( d_f \) - effective settling depth \([L]\),

\( P \) - total precipitate \((P_b + P_w)\) \([ML^{-3}]\), and

\( S \) - total sorbate \((S_h + S_w)\) \([ML^{-3}]\).

Assuming chemical processes also affect solutes in the storage zone, a similar set of equations are developed for the total storage zone component concentration, \(T_s\)

\[
\frac{\partial T_s}{\partial t} = \alpha \frac{A}{A_s} \left( T - P_b - S_b - T_s + P_{sb} + S_{sb} \right) + s_{ext} \quad (6)
\]

\[
\frac{\partial P_{sb}}{\partial t} = \frac{v_{p2}}{d_s} (P_s - P_{sb}) - f_{sb} \quad (7)
\]

\[
\frac{\partial S_{sb}}{\partial t} = \frac{v_{s2}}{d_s} (S_s - S_{sb}) - g_{sb} \quad (8)
\]

where

\( f_{sb} \) - source/sink term for dissolution from the storage zone immobile substrate,

\( g_{sb} \) - source/sink term for sorption/desorption from the storage zone immobile substrate,

\( s_{ext} \) - source/sink term representing external gains and losses to the storage zone,

\( v_{p2} \) - settling velocity for the storage zone precipitated phase \([LT^{-1}]\),

\( v_{s2} \) - settling velocity for the storage zone sorbed phase \([LT^{-1}]\),

\( d_2 \) - effective storage zone settling depth \([L]\),

\( A_s \) - storage zone cross-sectional area \([L^2]\),

\( P_s \) - total storage zone precipitate concentration \([ML^{-3}]\),

\( S_s \) - total storage zone sorbate concentration \([ML^{-3}]\),

\( P_{sb} \) - mobile storage zone precipitate concentration \([ML^{-3}]\), and

\( S_{sb} \) - mobile storage zone sorbate concentration \([ML^{-3}]\).

Solution of Equations - proceeds as follows. First, the chemical equilibrium model is called twice for each segment in the stream network. On the first call, the total component concentrations, \(T\), are supplied to the equilibrium model, and the total dissolved, precipitated and sorbed concentrations are

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calculated for the main channel. For the second call, the total storage zone concentrations ($T_s$) are used as input, and the various phases are determined for the storage zone in a similar fashion. Given the output from the equilibrium model, the source/sink terms ($f_b, g_b, s_b, s_{ext}$ and $s_{next}$) are computed as described by Runkel (1993). Equations (4), (5), (7) and (8) are then solved for $P_b, S_b, P_{sb}$ and $S_{sb}$, respectively, and Equation (2) is solved for $T$, using the Crank-Nicolson method and the decoupling procedure described by Runkel and Chapra (1993). Finally, Equation (6) is solved for the total storage zone component concentration, $T_s$.

**CONCLUSION**

The model presented here provides a descriptive tool for analyzing the fate and transport of trace metals in streams and rivers. Work is presently underway to incorporate additional capabilities, including an expanded analysis of sorption/desorption reactions and the consideration of iron redox processes.

**REFERENCES**


Simulation of Reactive Transport During a pH Modification Experiment in a Mountain Stream Affected by Acid Mine Drainage

By Robert E. Broshears,^1 Briant A. Kimball^2 and Robert L. Runkel^3

Abstract

A field experiment in a mountain stream in Colorado has helped to quantify hydrologic and chemical processes that control the transport of metals in water affected by acid mine drainage. Injection of sodium carbonate raised instream pH from 3.5 to a maximum of 5.8. Responses of aluminum and iron concentrations during the injection indicated the formation of aluminum and iron hydroxysulfate solid phases. Simulation of these responses using a reactive transport model reproduced the general aspects of observed patterns of concentration changes. Discrepancies between simulated and observed concentrations indicated the importance of chemical interactions between the water column and the streambed and kinetic restraints on the attainment of equilibrium.

INTRODUCTION

Diverse interactive physical, chemical, and biological processes affect the mobility and ultimate fate of metal constituents in surface water. The processes of advection, dispersion, precipitation/dissolution, sorption/desorption and oxidation/reduction contribute to the patterns of concentration observed in streams downgradient from contaminant sources such as acid mine drainage. While field measurements are necessary to characterize physical transport in streams, determination of chemical equilibria and rates of chemical and biological reactions is commonly relegated to the controlled conditions of the laboratory. An understanding of the natural world, however, requires that interactive processes be studied in the field, where the complexities of stream history, variable boundary conditions, and distributions of residence times in biogeochemical microenvironments combine in ways not duplicated in the laboratory.

This paper describes a field experiment conducted in Saint Kevin Gulch, a mountain stream receiving acid mine drainage near Leadville, Colorado (fig. 1). During the experiment, injection of sodium carbonate raised pH in the stream. Aluminum and iron concentrations in filtered samples decreased at higher pH values. These decreases in aluminum and iron were attributed to the precipitation of hydroxysulfate solid phases. In the case of iron, formation of these complexes apparently was favored by increased rates of oxidation at higher pH. The primary interpretive tool for the study was a reactive solute transport model called OTEQ (Runkel and others, 1996). OTEQ couples OTIS (Runkel and Broshears, 1991), an advection-dispersion model that includes transient storage, with MINTEQA2 (Allison and others, 1991), a model that calculates speciation under conditions of geochemical equilibrium.

EXPERIMENTAL METHODS

In August 1988, instream pH in Saint Kevin Gulch was increased step-wise from 3.5 to 5.8 by injecting a concentrated solution of sodium carbonate, with sodium chloride included as a conservative tracer. As the pulse of increased pH moved downstream, the
response of major ions and trace metals was documented by analyzing water samples collected at sites 1 through 4, located at 24, 70, 251, and 498 meters, respectively, from the injection point (fig. 1).

In describing the transport and fate of aluminum and iron, we distinguish two phases. The "filtered" phase remains in water passing through an 0.1 μm filter; the "particulate" phase is the concentration difference between an unfiltered sample and a filtered sample. The particulate phase may consist of solids that have aggregated into particles with a diameter greater than the nominal pore size. The particulate phase may also include constituents that have sorbed to these particles. The "total" concentration of each element is the sum of filtered and particulate concentrations. Metal concentrations were determined by inductively coupled argon plasma atomic emission spectroscopy on samples acidified in the field to less than pH 2.0 with ultrapure nitric acid. Concentrations of sulfate and other anions were determined by ion chromatography.

Figure 1. Map showing location of study area and sampling sites.
PHYSICAL TRANSPORT

Sodium was geochemically conservative throughout the experiment and was used as a tracer in defining physical transport. Injection of sodium carbonate and sodium chloride caused a distinct concentration pulse delineating the injection period (fig. 2a). The sequential arrival of the sodium pulse at each sampling site permitted definition of subreach travel times, while the asymmetry of the pulse allowed for the calibration of model parameters describing transient storage (Bencala and Walters, 1983; Stream Solute Workshop, 1990). Instream flow increased from 12.3 L/s at site 1 to 13.2 L/s at sites 3 and 4. Transient storage parameters were comparable to those developed in other studies of mountain streams (Broshears and others, 1993). Aluminum and iron were subject to the same regime of physical transport documented for sodium. By accounting for these processes in a rigorous manner, we were able to quantify the chemical and biological processes influencing aluminum and iron within the context of physical transport.

pH PERTURBATION

Prior to the experiment, background pH values were 3.4 to 3.5, with an increase to 3.8 at site 4. The injection began at 0900 hours and soon resulted in a pH of 4.2 at site 1 (fig. 2b). An increased injection rate begun at 1200 hours eventually resulted in a pH of 5.8 at this site. After the injection ended, pH at site 1 returned to near pre-injection levels. At the three

Figure 2a. Observed and simulated concentrations of sodium during experiment.
Figure 2b. Observed and simulated pH during the experiment.
downstream sampling sites, the pH pulse was subdued relative to the upstream profile. These observations suggested reactions that liberated protons as the perturbation was transported through the reach. Plausible reactions that liberate protons include hydrolysis of aluminum and iron. The streambed may also react directly with carbonate species to buffer the change in pH.

RESPONSE OF ALUMINUM

At site 1, the background concentration of filtered aluminum was about 3.1 mg/L. As pH increased from 3.5 to 4.2, the aluminum concentration at this site did not change (fig. 3). When pH increased above 5.0, the concentration of filtered aluminum declined substantially, reaching 0.01 mg/L at pH 5.8. The decrease in filtered aluminum was accompanied by an increase in particulate aluminum to a concentration of 3.1 mg/L. Thus, the total concentration of aluminum in the water column remained more or less unchanged. These observations were consistent with the formation of a nonsettling aluminum precipitate during the injection. A slight decrease in sulfate concentration during the same interval indicated that this anion may have been incorporated into the aluminum precipitate. After the injection stopped, filtered aluminum concentration increased and particulate aluminum concentration decreased, both eventually returning to pre-injection values. However, for approximately 30 minutes after the injection stopped, filtered aluminum concentration was higher than the background level. This spike in aluminum concentration suggested the return of aluminum into the water column from a pH-dependent source on the streambed.

Relative to site 1, sites 2-4 exhibited a smaller decrease in filtered aluminum concentrations during the interval of higher pH (fig. 3), and less particulate aluminum was formed. There was a slight decrease through time in total aluminum relative to pre-injection levels. The aluminum mass in the post-injection spike in filtered aluminum increased with downstream distance. These observations suggested the formation of a slowly settling aluminum precipitate, with decreasing rates of formation at the lower pH of the downstream sites. The spike in aluminum concentration likely was attributable to the dissolution of recently settled precipitate as the pH of the overlying water decreased following the injection.

RESPONSE OF IRON

Before the injection, background concentration of filtered iron declined gradually from 1.1 mg/L at site 1 to 0.75 mg/L at site 4 (fig. 4). Background particulate iron concentration was virtually unchanged along the reach. These observations were consistent with approximately equal rates of aggregation of iron-bearing chemical precipitates and physical settling of particulate iron along the reach. When pH increased to 4.2 at site 1, there was a slight decline in filtered iron (to 1.0 mg/L) and a concomitant increase in particulate iron (to 0.1 mg/L). As pH increased to 5.8, filtered iron decreased to 0.4 mg/L and particulate iron increased to 0.7 mg/L. Thus, total iron concentration in the water column at site 1 was conservative during the injection period. These observations were consistent with formation of a nonsettling iron precipitate at higher pH.

The concentration of filtered iron decreased in the downstream direction throughout the experiment (fig. 4). The pulse of particulate iron also diminished with downstream distance. These observations were consistent with a high rate of pH-dependent production of particulate iron immediately downstream from the injection and subsequent settling of particulate iron during transport to sites 3 and 4.

GEOCHEMICAL REACTIONS AND REACTIVE TRANSPORT SIMULATIONS

Relations between pH and concentrations of filtered metals and sulfate during the experiment were evaluated by Kimball and others (1994). Mass balance analyses were consistent with the formation of aluminum and iron hydroxysulfate solids with the following stoichiometry:

\[ \text{Al(OH)}_{1.96} (\text{SO}_4)_{0.52} \quad \text{and} \quad \text{Fe(OH)}_{2.23} (\text{SO}_4)_{0.38} \]

Calculated instream ion activity products for the proposed aluminum and iron solids were $10^{-2.34}$ and $10^{0.316}$, respectively.

For the OTEQ simulations, the carbonate boundary condition was adjusted to reproduce the observed pH at site 1; dynamic exchanges of carbon dioxide with the atmosphere were not modeled.
Figure 3. Observed and simulated aluminum concentration during the experiment.
Figure 4. Observed and simulated iron concentration during the experiment.
directly. The ferric iron boundary condition was varied to reflect changes in relative rates of photoreduction (McKnight and others, 1988; McKnight and Bencala, 1989) and pH-sensitive oxidation (Singer and Stumm, 1970) during the experiment. Only the aluminum and iron hydroxysulfate solids described above were allowed to precipitate and settle from the water column.

At site 1, simulated and observed values for pH, filterable aluminum and filterable iron were in general agreement. Differences between simulated and observed values increased in the downstream direction, as shown in the plots for sites 2-4 (figs. 2-4). The increasingly poor correspondence between simulated and observed pH values with downstream distance may be attributable to the importance of geochemical interactions between the water column and the streambed. Static simulations with MINTEQA2 support the presence of a large reservoir of potentially exchangeable hydrogen ions on the streambed under ambient conditions; these hydrogen ions could have provided a substantial buffering capacity during the experiment. Failure to simulate pH profiles in part explained the unsatisfactory simulation of aluminum concentration at downstream sites. Discrepancies between simulated and observed iron concentration indicated that iron concentration may have been controlled by a solid phase that was less soluble than the iron hydroxysulfate solid described above. Uncertainty in patterns of iron redox chemistry throughout the day also contribute to difficulties in modeling the speciation of this element.

A second source of disagreement between observed and simulated concentrations involved the post-injection spike of aluminum. Because equilibrium chemistry was assumed, simulated aluminum that settled to the streambed during intervals of higher pH dissolved immediately upon restoration of lower pH values. Compared with simulated profiles, measured spikes were more dispersed in time, indicating a kinetic restraint on dissolution of the freshly settled aluminum solid.

We remain optimistic that the fate and transport of trace metals in surface waters can be characterized by a reactive transport model. Simulations to date have demonstrated the importance of streambed processes and continue to direct attention to areas of needed research. Further work is warranted on such modeling, including a more rigorous conceptualization of chemical interactions between the water column and bed sediments and the incorporation of kinetic restraints on the attainment of equilibrium.

REFERENCES CITED


Difficulties with Intermediate-Scale Experiments for Studies of Iron Chemistry in Streams Affected by Acidic Mine Drainage

By Diane M. McKnight¹, Kenneth E. Bencala², Richard A. Harnish¹, and Robert L. Runkel¹

Abstract

Iron chemistry in streams affected by acidic mine drainage is driven by many dynamic processes, such as precipitation, dissolution, photoreduction of ferric iron and microbial oxidation of ferrous iron. These processes can be studied with a variety of approaches, ranging from controlled laboratory experiments to field, stream-scale perturbation experiments. Experiments that are intermediate between laboratory and field experiments using sediments and water from the Snake River have been conducted. These experiments have been useful in demonstrating the general nature of iron biogeochemistry. However, difficulties reproducing results occur both within and among experiments. The heterogeneous nature of the stream sediments and seasonal variations in trace phases of iron oxides confound interpretation of the results and limit the predictive value of such experiments.

INTRODUCTION

Numerous alpine and subalpine streams in the Rocky Mountains of the central United States are enriched in trace metals from natural weathering of pyrite and (or) from acidic mine drainage. In Colorado, an estimated 600 km of stream reaches are contaminated by acidic mine drainage, and much of this contamination originates from abandoned mines located on remote mountain sides (Moran and Wentz, 1974). In these streams, the rocks of the streambed are often covered with abundant hydrous iron oxides; accordingly, iron chemistry is important in understanding the geochemistry and ecology of these acidic mountain streams.

SITE DESCRIPTION AND METHODS

The experiments were conducted using streambed material and water from the Snake River, a small mountain stream in Summit County, Colo. (fig. 1). The Snake River is acidic (pH 3.2-4.5) and metal enriched from the weathering of disseminated pyrite in schist and gneiss in the eastern side of the watershed (Theobald and others, 1963). This stream has iron and...
aluminum concentrations comparable to streams affected by acidic mine drainage in the Colorado Rocky Mountains (McKnight and Bencala, 1990). The streambed is composed of cobbles coated with iron oxides, and some of the rocks contain pyrite (McKnight and Bencala, 1989). Hydrologic experiments using inorganic tracers have shown that flow through the hyporheic (substream) zone is continuously exchanging with flow in the open channel (Bencala and others, 1990).

Most of the experiments were conducted using streambed material and water collected from the SN2 site on the Snake River (fig. 1), which is located just above the confluence of the stream with Deer Creek. In the 1992 experiment, water and streambed material were also collected from the SN1 site about 2 km upstream from the confluence. Streambed material and water were collected before sunrise in 1985 and at midday in 1992 in plastic buckets and stored in the dark. Table 1 summarizes the experiments that were conducted.

Figure 1. The Snake River and Deer Creek watersheds, showing the area containing a bog iron-ore deposit.
Table 1. Summary of intermediate-scale experiments conducted in the Snake River.

<table>
<thead>
<tr>
<th>Process</th>
<th>Dates</th>
<th>Experimental Design</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microbial oxidation of ferrous iron</td>
<td>July 1985</td>
<td>Observe decrease in ferrous iron in the dark.</td>
</tr>
<tr>
<td></td>
<td>August 1992</td>
<td></td>
</tr>
<tr>
<td>Dissolution of iron oxide with a pH decrease</td>
<td>November 1984</td>
<td>Observe increase in iron concentration with serial</td>
</tr>
<tr>
<td></td>
<td>May 1985</td>
<td>exposures to low-pH water.</td>
</tr>
<tr>
<td></td>
<td>November 1985</td>
<td></td>
</tr>
</tbody>
</table>

For the oxidation experiments, rocks of variable size were placed on metal racks in 4-L glass beakers filled with stream water, which was stirred with a magnetic stirrer rotating below the rack. In the 1985 experiment, two beakers were first exposed to sunlight and then placed in the dark, and two were left in the dark. In the 1992 experiment, the beakers were filled with stream water collected at midday and then placed in the dark. The samples collected from the beakers were immediately filtered using a 0.4-μm Nuclepore filters and an Antlia filtration unit. The total dissolved iron and ferrous iron concentrations were determined by the 2,2 bipyridine colorimetric method (McKnight and Bencala, 1988).

The dissolution experiments were conducted on November 8, 1984; May 5, 1985; and November 7, 1985. The rocks and fine sediments were sequentially leached with stream water acidified with H₂SO₄ (pH 2.5 to ambient). The experiments were conducted indoors in duplicate; no incident sunlight was allowed to fall on the buckets. One liter of acidified stream water was placed with rocks and fine sediment in a 26 cm diameter plastic bucket and agitated for 5 minutes. The stream water was then poured from the bucket and replaced with another 1 L of stream water; aliquots were immediately filtered using GFC glass-fiber filters and an Antlia filtration unit. During the experiments, pH and Eh were measured with an Orion Model 701 pH meter and an Orion 967800 combination redox electrode. The samples were analyzed for iron by inductively coupled plasma spectrometry, and iron redox states were measured colorimetrically during the 1985 experiments.

RESULTS AND DISCUSSION

The design of the oxidation experiments was based on the premise that the bacterial populations that oxidize the ferrous iron in the Snake River reside in the epilithon—the layer of algae and bacteria that covers the streambed substrate. Because of the importance of hyporheic flow in these mountain streams, there is sufficient contact of water with the microbial populations in the streambed to accomplish substantial decreases in ferrous iron concentration over a period of several hours of darkness when there is no longer a source of ferrous iron from photoreduction.

The results of the two oxidation-rate experiments are shown in figures 2 and 3. In the 1985 experiment, a progressive decrease in ferrous iron concentration occurred when the sunlight-exposed beakers were placed in the dark. The initial iron concentrations were different in the two beakers that were maintained in the dark from the time of sample collection before sunrise. In the beaker that had the lower initial iron concentration, no decrease in ferrous iron occurred. However, a decrease occurred in the beaker with the higher concentration. The data showing a decrease in ferrous iron once the light-exposed beakers were placed in the dark was used to calculate an oxidation rate. This rate agreed reasonably well with the rate calculated from the decrease in ferrous iron in the stream itself at night (McKnight and Bencala, 1988).

In the 1992 experiments, no significant decrease of ferrous or total iron occurred during the experiments with water and rocks from either the main site or the upstream site. The results from duplicate beakers were very similar. The main difference in the design of the 1985 and 1992 experiments was that, in 1985, two of the beakers were initially exposed to sunlight, whereas in the 1992 experiment the water and rocks were taken directly from the stream and placed in the dark. A possible reason why this difference should account for the failure to observe oxidation of ferrous iron in the 1992 experiment is that there had been a longer period for populations of ferrous oxidizers to adjust to the experimental conditions in the 1985 study.

The most straightforward explanation for the difference in results of the experiments is that, in the 1992 experiment, the number of active ferrous oxidizing bacteria transferred with the streambed rocks was not adequate to cause a measurable decrease in ferrous iron during the 4-hour experiment. The rate of ferrous iron oxidation is only first order with respect to the ferrous iron concentration if there is a sufficient microbial population. If the beakers had been incubated for more than 3 hours, a microbial population might have developed to oxidize the ferrous iron.
Figure 2. Results of an oxidation rate experiment in the light and in the dark conducted in 1985 (modified from McKnight and Bencala, 1988).
Figure 3. Results of an oxidation-rate experiment in the dark conducted in 1992.
The results of the three dissolution experiments are presented in figure 4. In all three experiments, the iron concentrations were greatest at the lowest pH value, as would be predicted from chemical-equilibrium calculations. The results of these experiments also were generally consistent in showing that the dissolution of iron oxides with a decrease in pH was very rapid, occurring within the first 5-minute batch exposure. This rapid response is the same as was observed in an instream experiment in which the pH of the Snake River was lowered from 4.2 to 3.2 for a 3-hour period (McKnight and Bencala, 1989). In the stream experiment, photoreduction was an important process that presumably did not occur in these experiments. As in the oxidation experiments, the duplicate samples of streambed material gave similar results in the iron oxide dissolution.

In the detailed response, however, some significant differences between results of the experiments were observed, including some peculiar aspects of the iron speciation. One of the experiments done at the end of summer (November 8, 1984) took place when the hydrologic conditions were similar to those existing during the instream pH-perturbation experiment (McKnight and Bencala, 1989) and the pH was 3.92. In this experiment, an initial peak in the iron concentration resulted, which closely agreed with the instream experiment results, indicating the presence of a trace soluble-oxide phase. When the batch experiment was repeated at the same time the next year (November 7, 1985), the pH of the stream water was lower (pH 3.5) and the initial peak did not appear. The reason for this is probably that the soluble-trace phase represented in the initial peak evidenced in the instream experiment and the 1984 batch experiment would have already dissolved at this low pH.

The batch experiment was also conducted at the beginning of snowmelt (May 5, 1985), when most of the upstream reach of the Snake River was covered with ice and snow. The initial peak did not occur in this experiment either. The presence of the trace soluble-oxide phase may be related to the diel cycle of redox and precipitation/dissolution processes. Such a trace soluble-oxide phase may not be present in detectable quantities following extended periods under snow and ice without exposure to UV-radiation to drive the photochemical component of the diel cycle observed during periods of open water. Another difference between the spring batch experiments and the second fall batch experiment was that, in the spring, most of the released iron was ferrous iron, whereas in the fall, ferric iron was the predominant form and the ferrous iron concentration did not vary much with changes in pH. This result is intriguing, in that a reductant that is independent of sunlight is necessary to explain the ferrous iron in the spring experiment. One possible source of ferrous iron in this experimental system may be oxidation of pyrite by ferric iron released by dissolution of the iron oxide. The abiotic oxidation of pyrite by ferric iron is rapid. Trace amounts of pyrite have been found in streambed material from this site (McKnight and Bencala, 1988).

The results of the batch experiments consistently indicate an increase in dissolved iron with a decrease in pH. However, the results emphasize that detailed responses to a change in stream pH may vary seasonally, possibly because of variations in stream chemistry and in iron-containing solid phases in the streambed. These variations may be only weakly related to predictable seasonal changes, such as the development of an ice cover and decreases in pH at low flow. In order to predict reactive transport by means of a solute-transport model, the model would have to include important iron reactions and would have to accommodate changes in initial conditions, such as variability in concentrations and characteristics of solid phases. In addition to spatial variability, seasonal variability may constrain the predictive application of solute transport models.

**CONCLUSIONS**

Possible explanations have been presented that provide some insight into iron dynamics in the Snake River. However, the results of these experiments have the common feature of not being definitive. The variation in results of the different experiments was substantial and, although possibly attributable to variations in characteristics of streambed material, it would have been difficult to make the independent measurements of the characteristics that may have controlled the response, such as the abundance of a trace soluble phase of iron oxide or of viable ferrous oxidizing bacteria. Therefore, the overall conclusion is that the transition from the intermediate-scale to the stream-scale is, in some ways, more problematic than the transition from carefully controlled laboratory experiments to the stream scale.
Figure 4. Results of three dissolution experiments.
REFERENCES


Metal Concentrations in Sedges in a Wetland Receiving Acidic Mine Drainage from St. Kevin Gulch, Leadville, Colorado

By B.M. Erickson,¹ P.H. Briggs,¹ and T.R. Peacock¹

Abstract

As of the 1989 growing season, there were no visible signs of metal stress on the wetland vegetation receiving the acid mine drainage (AMD) from St. Kevin Gulch, Colorado. However, the AMD has affected the metal concentrations of the sedges growing on the wetland. Sedge concentrations of cadmium (Cd), copper (Cu), iron (Fe), lead (Pb), manganese (Mn), and zinc (Zn), known to be high in the AMD waters, are higher in the area of direct inflow than the sedge baseline geometric means (GM) reported for the wetland. Concentrations higher than the GM in other areas of the wetland are evidence for other sources of contamination to the wetland. Maximum cattle dietary levels reported in the literature for Cd (0.5 milligrams per kilogram (mg/kg)) and Zn (500 mg/kg) are exceeded in some areas of the wetland and could present a nutritional problem for the cattle grazing this wetland each year. Vegetation toxicity levels for Cu (20-100 mg/kg) and Pb (30-300 mg/kg) are not exceeded, but Pb concentrations are higher in the inflow area and may indicate accumulation is occurring. Fe deficiency, common in vegetation and foodstuffs, was not detected in the sedges of this wetland. Mn concentrations above the 500 mg/kg level reported in the literature as resulting in signs of visible stress in vegetation are exceeded in most areas of the wetland. The Fe/Mn ratio necessary for healthy vegetation (1.5-2.5), occurs only in the areas with the higher Fe concentrations. Presently the only element being removed from the AMD waters by the wetlands is Fe.

If the sedges accumulated higher levels of Fe, the ratio of Fe/Mn would not necessarily be improved. Fe and Mn are physiological antagonists, and at toxic Mn levels, the absorption of Fe process could reverse resulting in more stress and eventual loss of biomass.

INTRODUCTION

Acid mine drainage from St. Kevin Gulch, Leadville, Colo., drains into a 26-ha subalpine wetland. The wetland is a sedge meadow with two ecosystem components: (1) sedges growing on top of hummocks—the drier component (Carex canescens L.); and (2) sedges growing between or off hummocks—the aquatic component (Carex utriculata Boott.). The purpose of this study was to evaluate the affects of the AMD on the wetland sedges. To accomplish this purpose, two main tasks were identified. The first task was to establish the expected baseline trace-element concentrations in the sedges to delineate areas of possible effects. The second task was to examine seasonal variation and establish biomass production estimates to determine the amount of metals being removed from the AMD by the wetland. Baseline trace-element concentrations in Carex canescens and Carex utriculata can be found in Erickson and others (1991a;1991b). Seasonal results for all trace-elements and estimates of biomass production are currently being compiled. This paper presents Carex utriculata baseline and seasonal concentrations of Cd, Cu, Fe, Pb, Mn, and Zn. Data for Carex canescens are not included because the data resulting from both tasks indicated little statistical difference in metal concentrations between the two species.

¹U.S. Geological Survey, Denver, Colo.
STUDY PROCEDURES

The wetland was originally divided into 19 sampling cells, 122-m on a side, for the baseline task (fig. 1). Because the wetland is leased for cattle grazing, and samples of total growth were needed for the seasonal and biomass production estimates tasks, field enclosures were constructed in each of the 19 wetland cells in 1989 (fig. 1). Steel post and barbed-wire enclosures measuring approximately 1.8 m on a side were constructed. In the center of each exclosure, a 1-m diameter circle of flexible PVC tubing was secured with landscape pins to define the sampling area. Spring, summer, and fall samples were collected by

EXPLANATION

2 Baseline sampling cells
Acid mine-drainage inflow area
Elevated element concentration areas from baseline task
Poorly channelized flow
Seasonal sampling exclosures

Figure 1. Location of baseline sampling cells and seasonal sampling exclosures on the wetland receiving acid mine drainage waters of St. Kevin Gulch, Colo.
clipping the above-ground part of the two species of sedges from a different quarter of the circle for each season, bagged separately, and weighed in the laboratory.

In the laboratory, the sedge samples were washed in distilled water and dried in a forced-air oven at approximately 50 °C (degrees Celsius) for 1 week. A small set of sample splits were taken for estimates of variance due to preparation technique and (or) analytical precision. The samples were then pulverized and a small split of the raw material saved for atomic absorption analyses. The remaining sample material was ashed in a muffle furnace at 450 °C. All samples were weighed before and after ashing for percent-ash calculations. All samples were processed and analyzed in a random sequence to eliminate any systematic biases. Trace-element concentrations presented in this paper were determined on the ash by a 40-element inductively coupled plasma-atomic emission spectroscopy (ICP-AES) method developed by Crock and others (1983). Before statistical processing, all qualified values were replaced with a real value equal to 0.7 times the lower limit of detection according to methods described by Miesch (1976). All results were converted to dry-matter equivalents and converted to logarithms prior to statistical analysis. Summary statistics (tables 1 and 2) are reported as the geometric mean (GM), geometric deviation (GD), and baseline or expected range.

RESULTS

Baseline and Seasonal Comparisons

Conclusions reported in Erickson and others (1991b) for the baseline study are: (1) the greatest amount of variance in the trace-element concentrations between the sedges can be explained as the geographic differences between the 19 cells, (2) sedge samples, with trace-element concentrations above the baseline GM values, cluster at the inflow area of the St. Kevin Gulch AMD (fig. 1), indicating the vegetation has been affected, and (3) clusters of sedge samples with trace-element concentrations above the GM and occurring in other areas of the wetland are evidence that St. Kevin Gulch AMD is not the only source of contamination to the wetland (fig. 1).

Samples for the baseline task were collected in the fall of 1988. A comparison of the summary statistics for Cd, Cu, Fe, Pb, Mn, and Zn from the baseline task (table 1) to the fall seasonal results (table 2) shows that the baseline or expected range of concentrations for Cd, Mn, and Pb are similar. The differences in the concentrations of Cu, Fe, and Zn between the two tasks are probably due to the geographical difference between sampling sites. The baseline cell samples were collected from a 122-m² area, whereas the seasonal exclosure samples were collected within a 1-m-diameter circle.

The flow from St. Kevin spreads out in the areas of cells 9, 10, 8, 11, 12, 13, and 14 (fig. 1, inflow area), and Cd, Cu, Fe, Mn, Pb, and Zn concentrations in the baseline samples were higher than the wetland GM in this area. Seasonal sample data graphed in figures 2, 3, and 4 also illustrate increased element concentrations in the inflow area of the wetland. Higher concentrations on the graphs, in areas other than the inflow, tend to occur in the same cell areas as the baseline higher concentration clusters of figure 1.

### Table 1. Baseline summary statistics for metal concentrations in Carex utriculata collected within the 19 cells in the Leadville, Colo., wetland

<table>
<thead>
<tr>
<th>Element</th>
<th>Detection ratio</th>
<th>Geometric mean</th>
<th>Geometric deviation</th>
<th>Baseline or expected range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>38:94</td>
<td>0.34</td>
<td>2.00</td>
<td>0.09 - 1.3</td>
</tr>
<tr>
<td>Cu</td>
<td>94:94</td>
<td>6.20</td>
<td>1.70</td>
<td>2.1 - 18</td>
</tr>
<tr>
<td>Fe</td>
<td>94:94</td>
<td>270</td>
<td>1.90</td>
<td>78 - 930</td>
</tr>
<tr>
<td>Mn</td>
<td>94:94</td>
<td>320</td>
<td>1.70</td>
<td>120 - 860</td>
</tr>
<tr>
<td>Pb</td>
<td>58:94</td>
<td>0.96</td>
<td>2.40</td>
<td>0.17 - 5.5</td>
</tr>
<tr>
<td>Zn</td>
<td>94:94</td>
<td>170</td>
<td>2.30</td>
<td>32 - 860</td>
</tr>
</tbody>
</table>

### Table 2. Seasonal summary statistics for metal concentrations in Carex utriculata, collected within the 19 exclosures constructed on the Leadville, Colo., wetland

<table>
<thead>
<tr>
<th>Element</th>
<th>Detection ratio</th>
<th>Geometric mean</th>
<th>Geometric deviation</th>
<th>Baseline or expected range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>13:19</td>
<td>0.49</td>
<td>2.80</td>
<td>0.06 - 3.8</td>
</tr>
<tr>
<td>Cu</td>
<td>19:19</td>
<td>17</td>
<td>1.70</td>
<td>3.9 - 35</td>
</tr>
<tr>
<td>Fe</td>
<td>19:19</td>
<td>350</td>
<td>2.10</td>
<td>88 - 1400</td>
</tr>
<tr>
<td>Mn</td>
<td>19:19</td>
<td>420</td>
<td>1.70</td>
<td>144 - 1200</td>
</tr>
<tr>
<td>Pb</td>
<td>11:19</td>
<td>0.68</td>
<td>2.40</td>
<td>0.12 - 3.3</td>
</tr>
<tr>
<td>Zn</td>
<td>19:19</td>
<td>160</td>
<td>2.20</td>
<td>33 - 780</td>
</tr>
</tbody>
</table>

*Table 1. Baseline summary statistics for metal concentrations in *Carex utriculata* collected within the 19 cells in the Leadville, Colo., wetland*

*From Erickson and others (1991a). Concentrations are in milligrams per kilogram, dry-matter basis*

*Table 2. Seasonal summary statistics for metal concentrations in *Carex utriculata*, collected within the 19 exclosures constructed on the Leadville, Colo., wetland*

*Concentrations are in milligrams per kilogram, dry-matter basis*
Figure 2. Cadmium and zinc seasonal concentrations in Carex utriculata collected on the wetland receiving the acid mine drainage waters of St. Kevin Gulch, Colo.
Figure 3. Copper and lead seasonal concentrations in Carex utriculata collected on the wetland receiving the acid mine drainage waters of St. Kevin Gulch, Colo.
Figure 4. Iron and manganese seasonal concentrations in Carex utriculata collected on the wetland receiving the acid mine drainage waters of St. Kevin Gulch, Colo.
Seasonal Composition

Loss of biomass usually occurs before visible signs of metal stress appear in vegetation (Kabata-Pendias and Pendias, 1984). Within the boundaries of the wetland during the baseline (1988) and seasonal (1989) tasks, neither condition existed. However, baseline results indicate that Cd and Zn concentrations in sedge samples from the areas of inflow of St. Kevin AMD waters (fig. 1), South Spring, and outflow exceed the recommended cattle dietary levels (0.5 and 500 mg/kg, respectively) reported by Dollhopf and others (1990). Results for the Cd seasonal data (fig. 2) also indicate that cattle dietary levels are exceeded in the spring sedge samples collected in the exclosures located within the baseline wetland cells 10, 11, 13, 15, 16, 17, and 18. Summer sedge samples exceed the levels in exclosure samples from 10, 11, 15, 17, and 18. During the fall, Cd levels are exceeded in the sedge samples from the exclosures in cells 4, 10, 13, 14, and 17. With the exception of cell 4, all Cd concentrations exceeding the recommended levels for cattle occur in areas receiving St. Kevin AMD. The higher Cd concentrations in the exclosure samples from cell 4 are probably affected by the mine tailings located just north of the wetland (Walton-Day and Erickson, 1990). Fall concentrations of Zn exceed cattle dietary levels in the sedges from the exclosures in cells 4, 8, 10, 14, and 17. Spring exclosure samples exceed the Zn levels in cells 10 and 15. Zinc concentrations in the summer sedges are all below the 500 mg/kg level.

Kabata-Pendias and Pendias (1984), reported that normal levels of concentrations for Cu in vegetation are 5 to 30 mg/kg, deficient levels 2 to 5 mg/kg, and toxic levels 20 to 100 mg/kg, depending on species and other environmental parameters. All Cu concentrations in the seasonal sedge samples from the Leadville wetland were below toxic levels except the spring samples from exclosures in cells 10 and 18 (fig. 2). Fall concentrations of Cu appear to be in the deficient range, but there is a continuous decrease in concentration throughout the growing season, and Cu is known to be very mobile and to translocate back to the roots in the fall. This decrease in Cu concentration over the growing season was not observed in Carex aquatilis at Peru Creek, Colo., by Cooper and Emerick (1987). Differences in species and (or) substrate are two possible explanations.

Pb concentrations increase throughout the growing season, except in the samples from exclosures 10 and 18 (fig. 3). Emerick and others (1987), did not find an accumulation of Pb in sedges in the Peru Creek wetland study, but the comparatively high concentrations in cells 4, 10, 14, and 17 indicate that accumulation may be occurring in the area of AMD inflow on this wetland. The Pb concentrations in the sedges in this wetland are still below the 30–300 mg/kg toxic level for vegetation reported by Kabata-Pendias and Pendias (1984).

Vegetation uptake and transport of Fe do not occur readily; deficiency is generally the greater problem. Nutritional needs of cattle range from 50 to 100 mg/kg, and fodder concentrations can range from 18 to 1,000 mg/kg. Concentrations of Fe in figure 3 indicate deficiency is not a problem in this wetland. Fe toxicity in vegetation can occur, and when it does, it is usually in vegetation growing on strong acid soils, acid sulfate soils, or flooded soils (Kabata-Pendias and Pendias, 1989). Results from the study of the inflow and outflow water chemistry for this wetland indicate that Fe is presently the only metal being retained in the wetland (Walton-Day, 1991). Fe toxicity could occur in the future.

Mn is taken up and translocated rapidly in vegetation and is most mobile on acid and flooded soils. Normal concentrations for vegetation in general are between 30 and 300 mg/kg, but concentrations as high as 1,840 mg/kg in forage have had no adverse affects on cattle. Deficiencies can occur below 25 mg/kg and toxic affects on vegetation are often visible at concentrations over 500 mg/kg. Mn concentrations in the sedges from this wetland exceed the toxic threshold in all exclosures except 2, 3, 4, 11, and 17 (fig. 4) during some part of the growing season.

The Fe/Mn ratio necessary for healthy vegetation should range between 1.5 and 2.5 (Kabata-Pendias and Pendias, 1989). The only spring sample with a ratio between 1.5 and 2.5 was collected from the exclosure in cell 17. Summer samples from exclosures 1 and 3, and fall samples from exclosures 1, 6, 8, 13, 14, 16, and 17, had healthy Fe/Mn ratios. The greater number of samples with a healthy Fe/Mn ratio occurring in the fall, is probably related to the higher fall Fe concentrations, as shown in figure 4. Because Fe is the only element accumulating in the wetland, the wetland Fe/Mn ratio might be expected to improve in the future. However, further retention of Fe by the wetland could also increase the imbalance because Fe and Mn are physiological antagonists (Kabata-Pendias and Pendias, 1989). Deficient and normal Mn concentrations can both antagonize Fe absorption, and toxic levels can reverse the process. Because the 500 mg/kg Mn toxic level capable of causing visible stress in vegetation is already exceeded in the wetland sedges, loss of biomass could occur in the future.
SUMMARY

St. Kevin Gulch AMD has affected the vegetation of the wetland, but there were no visible signs of stress or loss of biomass during the 1988 and 1989 growing seasons. Baseline and seasonal task concentrations of Cd, Cu, Fe, Mn, Pb, and Zn in *Carex utriculata* were elevated above the GM in the area of inflow to the wetland. Results from the seasonal task also support the baseline task conclusion that St. Kevin is not the only source of contamination to the wetland. Cd and Zn concentrations exceed the recommended dietary levels for cattle in the areas of inflow of AMD and the outflow for the wetland. Cu and Pb do not present a problem at this time, but Pb might be accumulating in the area of inflow to the wetland. Fe deficiency in vegetation is not a problem in this wetland. The level of Mn that usually results in visible signs of stress is exceeded in most areas of the wetland, and the Fe/Mn ratio necessary for healthy vegetation occurs only in areas with higher Fe concentrations. Fe is the only element being removed from the AMD by the wetland, but continued Fe accumulation will not necessarily improve the Fe/Mn ratio in vegetation. Fe and Mn are physiological antagonists and at toxic Mn levels, the absorption of Fe process could reverse, resulting in more stress and eventual loss of biomass.

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Uraniferous Waters of Southeastern Colorado: A Function of Geology, Climate and Land Use

By Robert A. Zielinski and Sigrid Asher-Bolinder

Abstract

The effect of local geology and land-use practices on dissolved uranium in water is indicated by reconnaissance sampling of surface waters and some springs along the Arkansas River valley of southeastern Colorado. The rate of increase of uranium concentration with distance downriver increases markedly as the river flows from predominantly undeveloped lands underlain by igneous and metamorphic rocks to agriculturally developed lands underlain by marine shale and limestone. An additional abrupt increase in dissolved uranium is observed along the section of river where discharge is greatly reduced because of extensive diversions for irrigation and where remaining flow is largely composed of irrigation return water. Water collected along this last section of river is anomalously enriched in dissolved uranium compared to the average concentration reported in water from outside of the irrigated areas. As is commonly observed, dissolved uranium shows particularly strong positive correlation with specific conductance. Uranium also shows strong positive correlations with sodium, magnesium, sulfate and chloride that contribute heavily to total dissolved solids and specific conductance in these waters. Lithium, boron, strontium and selenium are also positively correlated with uranium. The combination of natural weathering of uranium-bearing soils and sediments, extensive soil leaching by irrigation return waters, and evaporative concentration in a semiarid climate produce concentrations of dissolved uranium that may threaten local water supplies.

INTRODUCTION

The U.S. Environmental Protection Agency (USEPA) is currently (1993) proposing the addition of a new primary drinking-water regulation for uranium (U) of 20 µg/L, with implementation scheduled to begin in 1996. If accepted, this standard may be exceeded in approximately 1,500 public water systems (United States Environmental Protection Agency Fact Sheet, 1991) and in untold numbers of unregulated private water supplies. The addition of a national water-quality standard for this previously unregulated trace element will produce exceptional demand for information regarding the present distribution of uraniferous waters as well as the geologic and land-use factors that can affect the concentration and chemical form of dissolved U. The largest and most current database for U in water is a product of the National Uranium Resource Evaluation (NURE) Program of the middle 1970's. Within the coverage of 2° quadrangle units evaluated by NURE, waters in the Western U.S., and particularly eastern Colorado, are noteworthy for consistently elevated concentrations of dissolved U. For example, the mean U concentration in ground water in the Lamar quadrangle of southeastern Colorado is 19.4 µg/L--a concentration two to four times that of ground water in most other NURE quadrangles in the Western U.S. (Shannon, 1979).

In 1991, the U.S. Geological Survey (USGS) Uranium/Radon Investigations Program began a study of uranium distribution and mobility in southeastern Colorado. The immediate goals of this study were to (1) evaluate the local bedrock and soils as sources for U, (2) identify the form of dissolved U and the geochemical controls on U solubility, (3) evaluate the potential for secondary enrichment of U in easily disturbed near-surface environments and (4) identify land-use practices that affect dissolved U in water.
As these goals are met, they will improve the ability to predict other areas where similar geology, climate, and land use combine to produce high concentrations of dissolved U in water that could threaten local water supplies. The prospects for addressing the causes of high concentrations of dissolved U in water will depend upon the extent that land-use practices affect U concentrations, and the degree to which these practices can be modified.

The area selected for detailed study is confined to the Arkansas River valley of southeastern Colorado and surrounding lands within approximately 20 km of the river. This area includes a reach of some 360 river miles (579 km) starting near Leadville, Colorado, and ending at the Colorado-Kansas border. The river traverses a variety of bedrock units that can be conveniently grouped according to geographic location—that is, predominantly Precambrian igneous and metamorphic bedrock in the mountainous terrain from Leadville to Cañon City, and predominantly Upper Cretaceous age marine shales and limestones on the High Plains east of Cañon City (fig. 1), this study; Tweto, 1979). The type and intensity of land use can be generally divided on a similar geographic basis. Mountainous areas are largely undeveloped but include small areas of mining activity or limited agricultural development. In contrast, the Arkansas River valley east of Cañon City has a 120-year history of intensive agricultural development sustained by a complex network of canals, temporary storage reservoirs, transmountain diversions and irrigation wells (Taylor and Luckey, 1974; Abbot, 1985). Open rangeland exists outside of irrigated areas, and an area of intensive urban development is centered at Pueblo. The study area, therefore, offers ample opportunity to investigate the effects of variable geology and land-use in a relatively constant semiarid climate.

This paper summarizes preliminary observations that were based on detailed examination of existing NURE data and reconnaissance sampling of surface waters and springs along the Arkansas River valley in April 1991. The results begin to define the extent and causes of uranium enrichment in local waters and to provide guidelines for defining the course of future study.

**SAMPLE COLLECTION AND ANALYSIS**

A total of 77 water samples were collected during a 2-week period in mid-April 1991. Sampling sites included 19 locations along the Arkansas River as well as the mouth of most of the tributary streams. Most of the samples (48) were collected by USGS Water Resources Division personnel from an established network of sites designed to monitor water quality and flow in the river and its major tributaries. The remaining water samples from smaller tributaries, springs, and two saline lakes were collected by the authors and associates to provide more complete coverage, to include some samples outside of irrigated areas, and to begin to assess U enrichment in standing bodies of water. Natural flows in April are representative of the early spring season and are a location-dependent mixture of ground-water seepage and early spring runoff. In irrigated areas, these natural flows are further affected by releases from storage reservoirs, diversions to irrigation canals, and return flow from initial stages of irrigation.

The specific conductance, temperature, and pH of water samples were measured in situ, and samples were filtered through 0.45-µm membranes at the time of collection. All water samples were analyzed for dissolved uranium by inductively coupled plasma-mass spectrometry (ICP-MS) (Date and Gray, 1985), for arsenic (As) and selenium (Se) by hydride generation-atomic absorption spectrophotometry (HGAAS) (Fishman and Friedman, 1985), and for alkalinity (as HCO₃⁻) by titration with standard acid. A subset of 39 samples from the eastern part of the study area also was analyzed for concentrations of dissolved anions by ion chromatography (Fishman and Pyen, 1979) and for concentrations of dissolved cations by inductively coupled plasma-atomic emission spectrometry (ICP-AES) (Lichte and others, 1987). Estimated precision for most reported elements is better than ±10% (relative standard deviation).

**RESULTS AND DISCUSSION**

Recasting of existing NURE data for the Lamar 2° quadrangle in southeastern Colorado (fig. 1) provides some preliminary information on the respective effect of geology and land use on dissolved U in water. Almost the entire quadrangle is underlain by Upper Cretaceous marine shale and limestone, although the southern quarter also includes some
Lower Cretaceous Dakota Sandstone (fig. 1). The most obvious difference between the southern quarter and the rest of the quadrangle is related to land use. The southern quarter includes the Arkansas River valley from near Manzanola to the Colorado-Kansas border and all the irrigated lands adjacent to the River, whereas the rest of the quadrangle consists of largely undeveloped rangeland.

Approximately 90 percent of the 825 sampled wells in the Lamar 2° quadrangle contain greater than 1 μg/L U (Shannon, 1979). For this discussion, a value of 1 μg/L is considered a reasonable detection limit. If this population is subdivided according to latitude, water from wells in the southern quarter of the quadrangle contain a markedly higher average U concentration (31.7 ± 42 μg/L) than water from wells in the rest of the quadrangle (18.6 ± 24 μg/L) (fig. 2). Only 276 of the well entries included well depths. If the comparison is limited to wells shallower than 100 ft (30.5 m), the population is reduced to 175 wells. The respective average U concentrations, in micrograms per liter, for this small subset are 38.5 ± 39 (59 wells) and 18.7 ± 23 (116 wells). The similarity of the averages in this subset to those of the entire population of sampled wells indicate that most of the wells with unreported depths also were shallow. An alternative, but less likely, explanation is that there is very little difference between the average U concentration in
Wells in Lamar Quadrangle Bounded by 38°15'-40°N Latitude and 102°-104°W Longitude

Number = 566
Mean = 18.61
Std. Deviation = 24.13
Median = 10

Wells in Lamar Quadrangle Bounded by 38°-38°15'N Latitude and 102°-104°W Longitude

Number = 170
Mean = 31.67
Std. Deviation = 42.15
Median = 15

Figure 2. Frequency distributions of uranium concentration in well waters from different parts of the Lamar quadrangle, Colorado. Data is limited to wells where ground water contains a uranium concentration greater than 1 microgram per liter (data from Shannon, 1979).

The average U concentration of 18 µg/L in ground water in the northern part of the Lamar quadrangle is considered representative of undeveloped ground water that has interacted with Cretaceous bedrock units and derivative soils, then it is informative to draw comparisons with U concentrations in ground water from Precambrian crystalline rocks. NURE data for 10 wells in the mountainous half of the Pueblo quadrangle west of Cañon City are too limited, but the concentration of U in water from 75 springs exceeds 1 µg/L and averages 9.9±22 µg/L (Shannon, 1978).

The above comparisons which are based on areally extensive sampling of broadly defined water types, indicates that geology and land-use practices can affect the concentration of dissolved U in the study area. A second more focused investigation of these effects is provided by the suite of surface-water and spring samples reported herein. These waters, collected in April 1991, under moderate-flow, prereunoff conditions, provide a relatively instantaneous snapshot of downriver changes in dissolved U with respect to changes in surrounding geology and land use. Sample locations and U-concentration data are summarized in figure 3.

For the purpose of discussion it is convenient to consider three distinct sections of river: In the uppermost section from Leadville to Cañon City, dissolved U in the Arkansas River gradually increased from less than 1 to 3.3 µg/L (fig.4). Low U concentrations in snowmelt-derived water are not greatly modified through contact with predominantly igneous and metamorphic bedrock and alluvium over 120 river miles (193 km). Some slightly elevated U concentrations in tributaries (5-20 µg/L) can be attributed to acidic mine drainage near Leadville and to drainage from volcanic and volcaniclastic rocks that host some uranium mines northwest of Parkdale. None of these local tributaries supplied enough dissolved U to "spike" dissolved U dramatically in nearby sampling sites along the Arkansas River.

In the 100-mile-long (161 km) middle reach from Cañon City to Manzanola, dissolved U in the river again increased regularly from 3.3 to 14 µg/L, but at a faster rate (fig.4). Tributaries and a few sampled springs contain moderate U concentrations (5-50 µg/L). We propose that generally higher U values in tributaries and more rapidly rising U concentrations in the Arkansas River reflect the transition to (1) Upper Cretaceous marine shale and limestone bedrock and (2) the beginning of irrigation practices (approximately 30 percent of the irrigated acreage borders this section). Our set of river sampling sites showed no particular effect of a former U extraction mill near Cañon City, or of urban development near the town of Pueblo.

In the final section of river from Manzanola to Lamar, the dissolved U concentration does not increase in a linear fashion and concentrations scatter...
within the 30 to 50 µg/L range. All the values plot well above the linear trend defined by the rate of U increase in the middle section of river (fig.4). Tributary and spring U concentrations are in the 20 to 100 µg/L range with some concentrations exceeding 100 µg/L (fig.3). This section of river is distinguished from the middle section by markedly decreased discharge (10-20 percent of that at Manzanola), and increased contribution of recycled irrigation-return waters to total discharge (Cain, 1985). The adage that "the Arkansas River ends at Manzanola" is based on the fact that water diversions create a near zero-flow condition during parts of the irrigation season. Below Manzanola a much greater percent of discharge is either directly delivered drain water, or irrigation return indirectly delivered through tributaries and ground-water seepage. Ground water recharged to the alluvial aquifer is further cycled to the surface by pumping from more than 1000 irrigation wells (Taylor and Luckey, 1974). We propose that surface waters sampled along this section of river and in adjoining tributaries contain concentrations of U and other dissolved constituents that were increased by virtue of their extensive use and reuse during irrigation. We further propose that the additional enrichment of U in river water can be estimated by comparing measured concentrations to those predicted by the upper linear trend of figure 4. The upper linear trend is based on the rate of U increase along the middle section of river that traverses similar rock types but supports less irrigation and is much less affected by irrigation-water return.

The upper linear trend of figure 4 predicts the downriver increase in dissolved U concentration under moderate-flow conditions and under less intensive agricultural development. This trend indicates that, prior to extensive irrigation along the Arkansas River valley, natural processes plus moderate irrigation could have generated 20 µg/L U water by the time the Arkansas River exited Colorado. Uranium concentration in water stored in the alluvial aquifer also must have increased considering that this water was recharged by a mixture of surface water containing as much as 20 µg/L U and ground water.
containing an average of 18 μg/L U. The predevelopment concentration of U in Arkansas River water cannot be estimated from our data, but concentrations could have approached the 18 μg/L ground-water average during periods of low flow when ground-water seepage provided a large component of total discharge.

Dissolved U in all 49 surface water and spring samples collected east of Cañon City shows a strong positive correlation (r= 0.82) with specific conductance (fig. 5) indicating that dissolved U is a soluble and mobile species that is largely conserved in solution. This relation, which is commonly observed in natural waters, suggests that the more easily measured property of specific conductance can be used to estimate the potential for high U concentration. Previous studies of temporal and spatial variation of specific conductance in the Arkansas River valley (Konikow and Person, 1985; Cain, 1987) may indirectly address probable historic variations of trace elements such as U. Increases in specific conductance are attributed to mineral dissolution and evaporative concentration, both of which are accentuated as surface waters are highly managed and reused during irrigation in semiarid climates.

Areally extensive sampling and a probable wide variety of applied water compositions make it difficult to separate the effects of evaporative concentration from mineral dissolution. Cheraw Lake, a highly saline closed-basin sink for irrigation return water, provides a probable extreme example of the local extent of U concentration by evaporation. The lake is located 12 km north of La Junta and at the time of sampling contained 230 μg/L U in surface water (fig. 3). This sample does not plot on figure 5 because of its unusually high specific conductance of 31,000 μS/cm. Unusually high specific conductance associated with dissolved U may indicate addition of salts washed in or blown in from marginal salt flats. Alternatively, some precipitation of U can occur under reducing conditions at the lake bottom. More detailed study, including sampling of local input seepage waters, is required to address these questions.

Summary statistics for 16 measured variables in 39 surface-water samples collected east of Cañon City are presented in table 1. Samples were chosen to span the range of specific conductance (Cheraw Lake outlier excluded). The large positive correlation between U and specific conductance is also accompanied by a large positive correlation of U with the major dissolved

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Figure 4. Uranium in Arkansas River water, April, 1991, plotted as a function of river mile from Leadville, Colorado. Visually fitted linear trends labelled a and b define different rates of increase of dissolved uranium concentration in two sections of river with contrasting geology and land use. Linear trend a is for a section of river underlain by igneous and metamorphic rocks and containing largely undeveloped lands. Linear trend b is for a section of river underlain by marine shale and limestone and containing agriculturally developed lands. (Abbreviation: μg/L U/mile , microgram per liter of uranium per river mile.)

Figure 5. Uranium concentration as a function of specific conductance for all surface waters and springs collected east of Cañon City, Colorado, April 1991. Surface waters collected west of Cañon City plot near the origin and are omitted for clarity.
species sodium, calcium, magnesium, sulfate, and chloride that strongly contribute to specific conductance. The minor elements lithium, potassium and strontium that have geochemical affinity with the major dissolved species also correlate with U. The minor elements boron and selenium, that are commonly concentrated in saline waters of the Western U.S., also correlate positively with dissolved U. A previous study (Mueller and others, 1991) documented elevated concentrations of Se in irrigation-drainage waters along the Arkansas River valley of Colorado. The apparent behavior of U as a "conserved" element in solution indicates that, in this setting, mobilization and transport of U dominate over precipitation or sorptive uptake. High solubility of U is expected in oxygenated alkaline-pH surface waters that contain sufficient concentrations of dissolved carbonate to stabilize dissolved U as uranyl carbonate complexes (Langmuir, 1978).

A less well-defined correlation is exhibited between U and pH, which rarely shows strong covariation with specific conductance, and between U and dissolved carbonate, silica and manganese, which are probably limited by precipitation of calcium carbonate, silica, and manganese oxides. Additional statistical calculations for smaller subsets of samples containing measurable Fe and Ba also show poor correlation of these elements with U, again indicating solubility control, probably through precipitation of Fe oxides and barite. Equilibrium-based, mineral-solubility calculations using the computer code PHREEQE (Parkhurst and others, 1980) indicate saturation of these waters with calcite, dolomite, quartz, ferric hydroxide, and barite, and undersaturation-to-saturation with gypsum.

### Table 1. Statistical summary of chemical data for 39 surface-water samples from the Arkansas River valley east of Cañon City, Colorado, collected April, 1991.

<table>
<thead>
<tr>
<th>Variable</th>
<th>n</th>
<th>Minimum</th>
<th>Maximum</th>
<th>Mean</th>
<th>Standard deviation</th>
<th>Correlation coefficient with U</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sp.Cond.(μS/cm)</td>
<td>39</td>
<td>229</td>
<td>8,000</td>
<td>2,681</td>
<td>1,983</td>
<td>0.84</td>
</tr>
<tr>
<td>pH</td>
<td>39</td>
<td>7.55</td>
<td>8.70</td>
<td>8.09</td>
<td>.25</td>
<td>-.37</td>
</tr>
<tr>
<td>SiO₂</td>
<td>39</td>
<td>1.3</td>
<td>34</td>
<td>15</td>
<td>6.9</td>
<td>.31</td>
</tr>
<tr>
<td>Sodium</td>
<td>39</td>
<td>9.0</td>
<td>1,000</td>
<td>259</td>
<td>265</td>
<td>.86</td>
</tr>
<tr>
<td>Potassium</td>
<td>39</td>
<td>1.0</td>
<td>36</td>
<td>6.9</td>
<td>6.8</td>
<td>.50</td>
</tr>
<tr>
<td>Calcium</td>
<td>39</td>
<td>26</td>
<td>580</td>
<td>240</td>
<td>147</td>
<td>.70</td>
</tr>
<tr>
<td>Magnesium</td>
<td>39</td>
<td>7.0</td>
<td>490</td>
<td>119</td>
<td>111</td>
<td>.77</td>
</tr>
<tr>
<td>Bicarbonate</td>
<td>39</td>
<td>95</td>
<td>625</td>
<td>283</td>
<td>102</td>
<td>.30</td>
</tr>
<tr>
<td>Sulfate</td>
<td>39</td>
<td>28</td>
<td>5,080</td>
<td>1,344</td>
<td>1,250</td>
<td>.82</td>
</tr>
<tr>
<td>Chloride</td>
<td>39</td>
<td>1.7</td>
<td>320</td>
<td>70.6</td>
<td>85.3</td>
<td>.87</td>
</tr>
</tbody>
</table>

### Major elements (milligrams/liter)

| SiO₂                      | 39  | 1.3     | 34      | 15    | 6.9    | .31                          |
| Sodium                    | 39  | 9.0     | 1,000   | 259   | 265   | .86                          |
| Potassium                 | 39  | 1.0     | 36      | 6.9   | 6.8   | .50                          |
| Calcium                   | 39  | 26      | 580     | 240   | 147   | .70                          |
| Magnesium                 | 39  | 7.0     | 490     | 119   | 111   | .77                          |
| Bicarbonate               | 39  | 95      | 625     | 283   | 102   | .30                          |
| Sulfate                   | 39  | 28      | 5,080   | 1,344 | 1,250 | .82                          |
| Chloride                  | 39  | 1.7     | 320     | 70.6  | 85.3  | .87                          |

### Minor elements (micrograms/Liter)

| Boron                     | 34  | <100    | 2,000   | 394*  | 404*  | .96*                         |
| Lithium                   | 39  | 28      | 540     | 129   | 124   | .87                          |
| Manganese                 | 28  | <20     | 620     | 75.3* | 127*  | .06*                         |
| Selenium                  | 35  | <1      | 68      | 14.9* | 13.0* | .79*                         |
| Strontium                 | 39  | 220     | 11,000  | 4,335 | 3,195 | .79                          |
| Uranium                   | 39  | 3.3     | 220     | 45    | 47    | 1.00                         |

### Less frequently detected elements (micrograms/Liter)

| Total Iron                | 13  | <50     | 200     | ------ | ------ | -.22                         |
| Barium                    | 22  | <40     | 870     | ------ | ------ | -.19                         |

1Other elements sought but consistently below detection limit (micrograms/Liter) include; silver(2), arsenic(2), beryllium(1), bismuth(10), cadmium(1), cobalt(3), chromium(1), copper(10), gallium(5), molybdenum(10), nickel(5), lead(10), tin(10), vanadium(6), zinc(3), and zirconium(1).
CONCLUSIONS

Preliminary reconnaissance sampling of surface waters along the Arkansas River valley of southeastern Colorado indicates the existence of both geologic and land-use controls on concentrations of dissolved U. A plot of U concentrations in the Arkansas River as a function of distance downriver displays abrupt changes in slope and degree of scatter of values that are attributed to the contrasting and sequential effects of (1) Precambrian crystalline bedrock and derivative soils/sediments, (2) Cretaceous sedimentary bedrock and derivative soils/sediments and the extensive irrigation thereof. U concentrations are consistently highest and show the most scatter in the section of river where flow is largely sustained by returns of multicycled irrigation water. As is commonly observed in natural waters, U correlates positively with specific conductance and with other major and minor chemical species that are not limited by major sorptive uptake or the solubility of mineral precipitates. In this setting, specific conductance serves as an easily measured, albeit approximate, predictor of dissolved U concentration because both properties increase as a function of solid/water interaction and evaporative concentration. In semiarid southeastern Colorado, natural weathering, soil leaching, and evaporative concentration can produce regional ground water with U concentrations near the proposed USEPA drinking water regulation of 20 µg/L. Locally extensive irrigation in the Arkansas River valley further elevates dissolved U concentrations and this combination of natural and manmade effects could compromise water quality for communities that derive drinking water from the alluvial aquifer.

REFERENCES


Dissolved Organic Compounds in the Mississippi River from Minneapolis-St. Paul, Minnesota to New Orleans, Louisiana

By Larry B. Barber, II¹, Jerry A. Leenheer², Wilfred E. Pereira³, and Mary A. Noriega²

Abstract

Dissolved organic contaminants were measured in water samples collected from the Mississippi River during four sampling surveys to assess spatial and temporal variability of these substances in the river. A hierarchical analytical approach was taken in which both broad spectrum and specific compound analyses were used. Specific indicators of sewage effluents included anionic surfactants and caffeine. These compounds were detected throughout the river, with maximum concentrations occurring near major cities. Other compounds such as volatile chlorinated hydrocarbons and ethylenediamine-tetraacetic acid, which are more indicative of industrial effluents, also were detected throughout the river. Specific organic compound concentrations in water were less than 50 micrograms per liter, and were controlled by a variety of environmental processes. Depending on the molecular structure of individual chemicals, they can be persistent in the Mississippi River or they can be removed by biodegradation, volatilization, or sorption.

INTRODUCTION

The Mississippi River (fig. 1), a source of public water supply for more than 100 cities, receives wastewaters containing a variety of organic compounds, some of which are detrimental to aquatic organisms and human health. Runoff and wastewater from urban areas, farms, factories, and individual households contribute organic compounds to the Mississippi River. The objective of this study was to (1) determine the distributions and concentrations of organic compounds along the entire length of the river, (2) evaluate the seasonal variability in contamination patterns, (3) evaluate the environmental processes that control the occurrence and fate of the contaminants, and (4) compare the present-day water quality of the river with historical water quality. This paper summarizes some of the major findings of the larger study, in particular the longitudinal distribution of select dissolved constituents.

APPROACH

Organic compounds in the Mississippi River were evaluated by collecting water and sediment samples between New Orleans, La., and Minneapolis-St. Paul (Twin Cities), Minn., during four sampling surveys done in June-July 1991 (summer), October-November 1991 (fall), February 1992 (winter), and March-April 1992 (spring). Midchannel grab samples of water were collected at about 10-mi intervals as the Research Vessel Acadiana traveled upstream from New Orleans to the Twin Cities. During the return to New Orleans, depth-and-discharge averaged water samples and composite bed sediment samples were collected. The water and sediment samples were analyzed for a variety of organic compounds, a few of which are presented here.

RESULTS

Dissolved organic carbon (DOC) has important geochemical implications because it has the potential to (1) increase the water solubility and facilitate the transport of organic contaminants, (2) alter rates of biodegradation, (3) form complexes with trace metals, and (4) react during water treatment to produce potentially toxic byproducts. The DOC longitudinal profiles (fig. 2a) show high concentrations (10-12 mg/L) in the upper Mississippi River (above the confluence with the Ohio River) that decrease downstream, a sharp
decrease in concentrations below the Ohio River, and relatively constant concentrations (3-4 mg/L) in the lower Mississippi River (between the confluence with the Ohio River and the Gulf of Mexico). The distribution of DOC was influenced by regional cycling of natural organic matter, which is affected by climate, vegetation, soil type, and biogeochemical factors.

The longitudinal distributions of specific contaminants such as methylene-blue-active-substances (MBAS), total organic halide (TOX), volatile organic compounds (VOC), ethylenediaminetetraacetic acid (EDTA), and caffeine along the Mississippi River were more variable, reflecting the effect of multiple inputs from municipal, industrial, and agricultural sources.
Methylene-blue-active-substances are a composite measure of total dissolved anionic surfactants including linear alkylbenzenesulfonates (LAS—the surface active ingredient of detergents), LAS biological metabolites and impurities, other synthetic-anionic surfactants, and natural organic compounds such as humic and fulvic acids. Because MBAS is an indicator of sewage contamination, there is a historical record of MBAS measurements dating back to the early 1950's that allows long-term trends to be assessed. MBAS was present throughout the Mississippi River and its tributaries at concentrations ranging from 0.025 to 0.090 mg/L (fig. 3). Peak MBAS concentrations were detected in the vicinity of major cities as the result of sewage-effluent discharges, and concentrations rapidly decreased downstream as a result of dilution, biodegradation, and sorption to sediments. The results of LAS-specific analyses for water from the Mississippi River, and the biogeochemical processes that control their fate are reported by Tabor (1993) and Tabor and Barber (1996).

Total organic halogen is a measure of dissolved chlorinated organic compounds (volatile and non-volatile) that originate from disinfection of sewage effluents, biofouling control in powerplant-cooling waters, and pulp-wood bleaching. Although the composition of TOX is variable, it is an index of impairment of water quality as indicated by the toxicity.

Figure 2. Longitudinal distribution of dissolved organic carbon for midchannel water samples collected during three upriver surveys of the Mississippi River during 1991-92.
of many compounds determined by this measurement. The TOX concentrations in the Mississippi River ranged from 10 to 120 μg/L and showed significant seasonal differences (fig. 4). TOX is thought to be relatively resistant to removal by sorption and biodegradation.

Caffeine, a chemical in beverages such as coffee and soft drinks, was used as a specific tracer of domestic wastewater. Caffeine concentrations indicated the input of sewage from the Twin Cities into the relatively low volume upper Mississippi River and progressive dilution downstream (fig. 5). The Illinois River contained elevated concentrations of caffeine probably derived from the large population in Chicago, Ill. An increase in caffeine concentrations was detected in the Mississippi River below its confluence with the Illinois River.

Ethylenediaminetetraacetic acid is used to form water soluble complexes with insoluble metals and, as a consequence, has found use in a wide variety of domestic and industrial applications. The EDTA longitudinal profile indicates the upper Mississippi River had greater EDTA concentrations than did the lower Mississippi River (fig. 6). EDTA and caffeine are present in similar concentrations in sewage effluent; however, industrial sources and the lack of instream degradation probably produce EDTA concentrations in the Mississippi River that are higher than those of caffeine.
Volatile organic compounds such as trihalomethanes, chlorinated ethenes and ethanes, and aliphatic and aromatic hydrocarbons come from industrial and municipal sources, as well as petroleum fuel used in transportation. Many VOC's are U.S. Environmental Protection Agency priority pollutants and have maximum contaminant levels (MCL's) that range from 2 to 200 μg/L depending on the particular compound (U.S. Environmental Protection Agency, 1987). Thirty-two VOC's were detected and 19 were present in more than 1 percent (up to 15 percent) of the samples analyzed; about 23 percent of the samples had detectable VOC's. The most frequently detected compounds were dichloroethane, methylene chloride, toluene, trichloroethane and tetrachloroethene. Concentrations for these compounds ranged from 0.2 to 1.1 μg/L (typically an order of magnitude below MCL's for the individual compounds); the only reaches of the river with significant levels of VOC were below the Twin Cities, below the confluence with the Ohio River, and between Baton Rouge and New Orleans, La. (fig. 7). Loss of VOC's from the water as the result of volatilization appears to be a rapid process.

Figure 4. Longitudinal distribution of dissolved total organic halogen for midchannel water samples collected during three upriver surveys of the Mississippi River during 1991-92.
Figure 5. Longitudinal distribution of dissolved caffeine for depth and discharge integrated water samples collected during three downriver surveys of the Mississippi River during 1991-92.

Figure 6. Longitudinal distribution of dissolved ethylenediamine tetraacetic acid for depth and discharge integrated water samples collected during three downriver surveys of the Mississippi River during 1991-92.
Figure 7. Longitudinal distribution of volatile organic compounds for midchannel water samples collected during three upriver surveys of the Mississippi River during 1991-92.
DISCUSSION

The organic compounds in the Mississippi River comprise a complex mixture of a wide range of natural and synthetic chemicals introduced by a variety of sources. Although concentrations of most contaminants measured in this study were below U.S. Environmental Protection Agency regulatory limits, their presence was detected along the entire Mississippi River. Significant sources of organic compounds in the Mississippi River include municipal-wastewater discharge, urban runoff, powerplant cooling-water discharge, pulp-mill effluent, feedlot runoff, commercial and recreational river traffic and spills during refueling, and discharge from industrial facilities.

Although dissolved contaminant concentrations measured in this study indicate the potential for adverse effects, the Mississippi River is dynamic, and concentrations are continually changing; locations in the immediate vicinity of point sources such as municipal discharges are most likely to have the highest concentrations and largest number of organic compounds. It is difficult to relate concentrations in the river water to drinking water standards because water treatment can remove or introduce contaminants.

Distinct spatial patterns were observed in the organic-chemical data. The highest concentrations of organic compounds were in the vicinity of major metropolitan areas, and concentrations were typically greatest in the upper Mississippi River where stream dilution was lowest. The organic chemistry of major tributaries such as the Minnesota, Illinois, Missouri, and Ohio Rivers significantly affected the chemistry of the Mississippi River. Seasonal differences in organic compound concentrations are related to hydrologic, climatic, biological, and geochemical factors. Concentrations were highest during periods of low flow (fall) and lowest during periods of high flow (spring). Likewise, concentrations of biologically labile and volatile organic compounds were affected by temperature with highest concentrations in the winter, when temperatures were lowest. Depending on the molecular structure of the individual chemicals, some compounds were quite persistent in the Mississippi River, whereas others were rapidly removed by biodegradation, volatilization, and sorption. Although the results from this study represent a significant step forward in understanding the occurrence and nature of organic compounds in the Mississippi River, there still is much to be learned about their sources, fate, and effects on human health and aquatic ecology.

REFERENCES


Abstract

Linear alkylbenzene sulfonate (LAS), the active component in most detergents, is one of the most common synthetic organic compounds found in natural waters and sediments. The estimated LAS loading in the Mississippi River basin is 3,500 kilograms per day. A detailed sampling program was undertaken by the U.S. Geological Survey to determine the occurrence and fate of LAS in a 2,800 kilometer section of the Mississippi River from Minneapolis, Minn., to New Orleans, La. LAS was identified and quantified in 22 percent of the water samples at concentrations ranging from 0.06 to 28.2 micrograms per liter. Most dissolved LAS was associated with the sewage treatment plant outfalls of large cities along the river. LAS was identified in all of the composite bottom sediment samples at concentrations of 0.01 to 20 milligrams per kilogram. Sorption to sediment removes 5 to 30 percent of dissolved LAS. On the basis of homolog and isomer data, biodegradation is the most important removal process affecting dissolved LAS.

INTRODUCTION

Linear alkylbenzene sulfonate (LAS) is the world's most widely used synthetic surfactant. LAS consumption totaled 390 x 10^6 kg in the United States in 1991, 88 percent of which was used in detergents and household cleaners (Modler and others, 1993). Rapaport and Eckhoff (1990) estimate that each person in the United States uses about 2.6 g of LAS daily.

Most LAS is disposed of into municipal wastewaters and subsequently treated at sewage-treatment plants (STP). Most STP use secondary sewage treatment during which an average of 98 percent of LAS input is removed. Removal occurs by either (1) sorption to sludges or (2) biological degradation to intermediate compounds or ultimately to water, carbon dioxide, and sulfate ion (Rapaport and Eckhoff, 1990; Berna and others, 1989). Despite the high removal rate, significant amounts of LAS can be introduced into surface waters through discharge of municipal sewage effluent. Estimated LAS use in the Mississippi River basin is 175,000 kg/d (Tabor, 1993). Therefore 3,500 kg of LAS could be introduced daily to the Mississippi River and its tributaries.

This study was designed to evaluate the occurrence and fate of LAS in a 2,800 km reach of the Mississippi River between Minneapolis, Minn and New Orleans, La. The work reported here was part of the U.S. Geological Survey's 5-year study of contaminants in the Mississippi River (Meade, 1993) and is a summary of the master's thesis of Tabor (1993).

Study Area

The Mississippi River is the largest river in North America (fig. 1) and is the sixth largest river in the world based on annual discharge (Milliman and Meade, 1983). Its watershed covers 3.3 x 10^6 km^2 and drains 41 percent of the area of the 48 conterminous states (Turner and Rabalais, 1991). The upper river consists of a series of 27 locks and dams beginning about 10 km upriver from St. Louis and ending in the Minneapolis/St. Paul area. The lower section of the river is free-flowing to the Gulf of Mexico. Major tributaries include the Minnesota, Illinois, Missouri, Ohio, and Arkansas Rivers.

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Linear Alkylbenzene Sulfonate

Commercial LAS is a mixture of homologs having alkyl chain lengths ranging from 10 to 14 carbon units with isomers of variable phenyl position. The phenyl positions range from 2 to 7 for C_{10} to C_{14} LAS, resulting in a total of 26 isomers. The variable length of the unsubstituted alkyl chain causes each isomer to have slightly different characteristics relating to sorption and biodegradation. LAS has an aqueous solubility of 0.2 to 160 mg/L and a distribution coefficient (K_d) of <1000 to 6000 L/kg (Marcomini and others, 1988). This wide range of physical properties makes LAS an ideal indicator of environmental processes occurring in water and sediment.
EXPERIMENTAL

Field Sampling

Water and sediment samples were collected from the Research Vessel ACADIANA on three cruises in the summer (June 23-August 7) and fall (September 24-November 13) of 1991 and the spring (March 25-May 10) of 1992. Samples were collected from the Mississippi River between Minneapolis, Minn. and New Orleans, La. Tributaries having at least 5 percent of the discharge of the Mississippi also were sampled. Surface grab samples were collected on each upriver cruise, and composite water and sediment samples were collected on each subsequent downriver cruise. Details of the sampling procedures can be found in Meade (1993).

Analytical

LAS was identified using a solid-phase-extraction/derivatization/gas-chromatography/mass-spectrometry method adapted from Trehy and others (1990). LAS was isolated using a C₁₈ solid-phase extraction cartridge. LAS was derivatized to its trifluoroethyl ester and subsequently analyzed using a Hewlett-Packard gas chromatograph with electron impact mass selective detector. Quantitation was accomplished using a C₉ LAS surrogate standard added to each sample before isolation. LAS identification was based on the retention times and mass spectra of U.S. Environmental Protection Agency LAS standard #1288.

RESULTS AND DISCUSSION

Dissolved Linear Alkylbenzene Sulfonate

Dissolved LAS was found in 22 percent of the 437 water samples at concentrations of 0.06 to 28.2 µg/L. Spatial distribution of dissolved LAS in grab samples is shown in figure 2. Maximum concentrations of dissolved LAS in the Mississippi River were found below the STP outfalls of municipalities such as Minneapolis and St. Louis. Concentrations decreased with increasing distance from the outfall. Seventy-two percent of dissolved LAS was found within 65 km of the sewage outfalls of towns and cities along the river. Several tributaries contained measurable concentrations of LAS. Most of the water samples containing LAS were collected

![Figure 2](image-url)
from the Mississippi River above its confluence with the Ohio River, indicating that dilution is a secondary factor that determines LAS concentration in the river. Calculations based on the homolog and isomer distributions of dissolved LAS measured in the river indicated that biodegradation is the most important control of dissolved LAS in the Mississippi.

**Sorbed Linear Alkylbenzene Sulfonate**

LAS was identified in all 29 Mississippi River composite bottom-sediment samples in concentrations of 0.01 to 0.95 mg/kg (dry weight). Of the four tributaries sampled the highest concentration of sorbed LAS found was 20 mg/kg in Pig's Eye Slough, a canal that transports the Minneapolis/St. Paul sewage effluent to the Mississippi River. The highest sorbed LAS concentrations in the Mississippi River were found within 60 km of the Minneapolis area. The ubiquitous sorption of LAS to bottom sediments indicates that sorption is an important removal process of dissolved LAS. Calculations indicate that 5 to 30 percent of dissolved LAS may be removed from the river by sorption.

**SUMMARY**

Most LAS in the Mississippi River originates from the sewage outfalls of cities and towns located near the river and its tributaries. Dilution is an important control of LAS concentrations in the river. Sorption and biodegradation are the main controls on the fate of LAS in the river. LAS is a ubiquitous component of the bottom sediments, indicating that sorption plays a significant role in removal of LAS from the dissolved phase. Dissolved LAS homolog and isomer distributions indicate that biodegradation is the most important removal process of dissolved LAS. Biodegradation is the ultimate fate of LAS in the Mississippi River.

**REFERENCES**


Organic Carbon Associated With Suspended Silt and Colloid From the Mississippi River and Some of Its Tributaries, July 1991-May 1992

By Colleen E. Rostad\textsuperscript{1}, Stephanie G. Monsterleet\textsuperscript{1}, LaDonna M. Bishop\textsuperscript{1}, and Geoffrey S. Ellis\textsuperscript{1}

Abstract

Suspended silt and colloid samples were collected from 16 sites along the Mississippi River and from some of its tributaries during July-August 1991, October-November 1991, and April-May 1992 to determine the organic carbon associated with the suspended matter. Sample collection involved pumping discharge-weighted volumes of river water from a cross section of the river into a continuous-flow centrifuge to isolate the suspended silt. Colloid remaining in the aqueous phase was isolated by ultrafiltration. This is the first time that the presence of organic carbon associated with the suspended silt and colloid has been investigated along the entire reach of the Mississippi River from near Minneapolis, Minnesota, to south of New Orleans, Louisiana. The organic carbon content associated with the colloids (4 to 31 percent) was much higher than the organic carbon associated with the silt (1 to 17 percent).

INTRODUCTION

Depending on their water solubility, organic contaminants in a river system can be located in any of several compartments, such as water, silt, colloid, bed sediment, or benthic plants and organisms. The more water-soluble compounds are shown to be transported in the water phase (Pereira and Rostad, 1990; Pereira and others, 1990), whereas the less water-soluble compounds would be associated with organic carbon and would be transported with the organic carbon associated with the suspended matter--either the silt or the colloid.

Samples of silt and colloid were collected along the Mississippi River from near Minneapolis, Minnesota, to south of New Orleans, Louisiana. The sampling sites included four tributaries--the Minnesota, Illinois, Missouri, and Ohio Rivers. Sampling cruises were made during July-August 1991, October-November 1991, and April-May 1992. The summer and fall cruises were made during periods of low flow, in contrast to the spring cruise, which was made during high flow on the Mississippi River.

The purpose of this paper is to describe the distribution of organic carbon associated with the suspended silt and colloid at selected sites on the Mississippi River and some of its tributaries for these three cruises.

SAMPLE COLLECTION

Representative, discharge-weighted, suspended-matter samples were collected using techniques described by Moody and Meade (1992). Discharge-weighted samples are proportional to the discharge at each evenly spaced vertical of the cross section of the river at each site. The sampling sites for each cruise are shown on a map of the Mississippi River area in figure 1.

At each sampling site, the water discharge was estimated at each of from 5 to 30 (depending on the width of the river) equally spaced verticals along a cross section of the river by using the depth profile of

\textsuperscript{1}USGS, Arvada, Colo.
Figure 1. Map showing sampling sites on the Mississippi River and some tributaries. (* denotes a tributary)
the river and five depth-integrated velocity measurements. The 17-m research vessel ACADIANA, from which the samples were collected, was positioned in the river at each of the verticals of the river cross section by using microwave trisponders located on each bank. The maximum possible sampling depth for the equipment was 5 m. The discharge-weighted pumped sample was collected at each vertical from one-half the depth or 5 m, whichever was less.

The water was pumped through FEP Teflon tubing, rigidly positioned parallel to the flow, by an air-driven, double-diaphragm Teflon pump, into a 63-μm nickel-mesh sieve. The water then flowed into a large (40 L) glass funnel, which provided constant head pressure into a continuous-flow, high-speed centrifuge. The centrifuge was operated at 16,000 rpm (relative centrifugal force (RCF) of 15,000 gravities) and is described in detail by Leenheer and others (1989) and Rees and others (1991). To ensure high recovery efficiency of suspended silt, 2-L/min flow rate through the centrifuge was used; this rate was one-half that used by Ongley and Blachford (1982), who reported preferential losses of the organic-rich portion of the suspended sediment over the mineral-rich portion at a flow rate of 4 L/min. Particles as small as 370 nm were recovered in the centrifuge (Rees and Ranville, 1990).

All exposed centrifuge surfaces were coated with or directly machined from TFA or FEP Teflon to minimize sample contamination. Porous TFE Teflon was avoided throughout the sample isolation because it absorbs trace organic compounds and can retain contamination between sites. The suspended silt from a total of 500 to 1,000 L of water was deposited on the cylindrical wall of the centrifuge bowl, which was lined with a removable sheet of 0.35-mm-thick FEP Teflon. The liner was easily transferred from the bowl, using Teflon tweezers and FEP Teflon gloves, into an FEP Teflon sample bag, where the silt sample was resuspended by gentle massage of the liner from outside the bag. The suspended silt from the 500 to 1,000 L of river water was then contained in 1 to 2 L of water. This solution was transferred to 1-L glass jars, preserved with five drops of chloroform, transported on ice to the laboratory, allowed to settle for at least 1 week, aspirated to remove the supernatant, and air dried in the original container. The air-dried silt resulting from the sampling process was ground in a glass mortar, weighed, and mixed well. A portion was taken for organic-carbon analysis.

Colloid remaining in the aqueous phase was isolated by ultrafiltration through 30,000-molecular-weight cellulose filters. The colloid on the filter plates was placed in Teflon bags and resuspended using gentle external massage. The approximately 2 L of colloid in aqueous suspension was transferred to a 2-L Teflon bottle and transported on ice to the laboratory after two drops of chloroform was added. The sample was transferred to freeze-dry flasks, frozen, and freeze dried. A small portion of the fluffy colloid was used for organic carbon analysis.

RESULTS

The colloid accounted for about 10 percent by weight of the total suspended matter (silt and colloid) for most of the river in the summer. In the fall, the proportion of colloid increased to 20 percent at most sites and 35 percent at two upper river sites. During spring, the percentage of colloid by weight of the total suspended matter remained high in the upper river, but decreased to 5 percent in the lower river.

The organic carbon content, in percent, associated with the silt and colloid at each site is shown in figure 2a for the July-August 1991 cruise, in figure 2b for the October-November 1991 cruise, and in figure 2c for the April-May 1992 cruise. The samples were analyzed by Huffman Laboratories, Golden, Colo. The organic carbon content of duplicate samples varied less than 2 percent from the mean value.

At almost every site, the organic carbon content associated with the colloid (4 to 31 percent) was significantly higher than that associated with the silt (1 to 17 percent). The organic carbon associated with the silts averaged 4.1 percent in summer, 5.5 percent in fall, and 4.9 percent in spring; the organic carbon associated with the colloids averaged 16.5 percent in summer, 16.1 percent in fall and 13.0 percent in spring. Tributaries with high suspended-sediment concentration, the Minnesota River (site 2) and the Missouri River (site 11), usually had lower organic carbon content, associated with both the silt and the colloid, than did other nearby sites. During April-May 1992, the organic carbon content was consistently higher at the upstream sites (sites 1-7 on figure 2) than at the downstream sites, especially with respect to the colloid. The Ohio River, which supplies as much as half of the water to the lower Mississippi River, carried colloid with higher organic carbon content than that of nearby sites.
Figure 2. Percent organic carbon associated with the silt and colloid (A) July-August 1991, (B) October-November 1991, (C) April-May 1992.
The organic carbon content associated with the colloids averaged 15.2 percent. This percentage is substantially higher than that assumed in previous colloidal studies. Estimates of colloidal organic carbon content by Pankow and McKenzie (1991) were 10 percent for river headwaters and lake water, and 5 percent for rivers downstream of agriculture. The river headwater in this study (site 1) had colloidal organic carbon content averaging greater than 25 percent, when not under ice in April-May. Colloid from sites along the lock-and-dam lake system, such as sites 4-7, had consistently higher organic carbon content than colloid from the free-flowing river sites 14-16.

Hydrophobic or non-water-soluble compounds which associate with organic carbon will have more organic carbon available associated with the colloid than with the silt in the river. It is likely that the colloid will contain higher amounts of these compounds than the silt.

**SUMMARY**

Organic carbon associated with silt and colloid are reported from 16 sites along the Mississippi River and some of its tributaries; the samples were collected during July-August 1991, October-November 1991, and April-May 1992. This is the first time that the organic carbon associated with the suspended silt and colloid has been reported for the entire reach of the Mississippi River from near Minneapolis, Minnesota, to south of New Orleans, Louisiana. Colloidal organic carbon content has not been reported previously. Because hydrophobic compounds partition into organic carbon, the colloidal transport of hydrophobic toxic organic compounds may be as important as their silt transport in the Mississippi River.

**REFERENCES**


Accumulation of Organochlorine Compounds in *Hydrilla Verticillata* Relative to Sediments in the Tidal Potomac River

By Jessica A. Hopple and Gregory D. Foster

Abstract

Submersed aquatic plants are a sink for hydrophobic organic compounds. An average accumulation of 71 micrograms per kilogram of polychlorinated biphenyls was measured in *Hydrilla verticillata* collected from the freshwater reach of the tidal Potomac River, and an average of 53 micrograms per kilogram was measured in the bed sediment at the same location. *Hydrilla verticillata* accumulated an average of 1.60 micrograms per kilogram and the bed sediment accumulated an average of 0.77 micrograms per kilogram for each of the five chlorinated pesticides measured. Accumulation of chlorinated pesticides and polychlorinated biphenyls in *Hydrilla verticillata* was found to be a significant factor in the redistribution of contaminants in the tidal Potomac River.

INTRODUCTION

Organochlorine pesticides and polychlorinated biphenyls (PCB's) are nonpolar, hydrophobic organic compounds with large octanol/water partition coefficients (log $K_{OW} > 4$) and have been shown to partition from water onto sediments in aquatic systems (Elzerman and others, 1987). Stamer and others (1984) reported mean PCB concentrations of 152 µg/kg in the bed sediments of the Schuylkill River Pennsylvania, where the concentrations in water were usually below detection limits (1.0 µg/kg).

The Potomac River, Washington, D.C., is the second largest source of water to the Chesapeake Bay, contributing 18 percent of the total freshwater flow (Hickman, 1984). The tidal river has a deep channel with wide shoals on either side; the sides contain abundant submersed aquatic vegetation (Carter and others, 1987). An estimated 26 to 30 kg of PCB's are transported from the upper Potomac River to the tidal Potomac River each year (Foster, 1992).

The purpose of this study was to explore the accumulation of chlorinated pesticides and polychlorinated biphenyls (PCB's) in *Hydrilla verticillata* relative to bed sediments in the tidal Potomac River. Samples were collected from two sites in October 1991 and July 1992 and analyzed for PCB's and selected organochlorine pesticides using gas chromatography. The results of this study will help to determine whether the accumulation of the contaminants in plants will have an effect on the transport of hydrophobic organic compounds from the upper Potomac River to the Chesapeake Bay. Autumn senescence of *Hydrilla verticillata* and transport downstream of the released particulate material may be an important means of bulk transport from the area.

MATERIALS AND METHODS

Samples were collected from two sites in the tidal Potomac River south of Washington, D.C., Piscataway Bay and Greenway Flats (fig. 1). Piscataway Bay is located about 13 km south and Greenway Flats is located about 22 km south of the Blue Plains Sewage Treatment Plant on the east side of the Potomac River. Piscataway Bay is located near the mouth of Piscataway Creek.
Hydrilla verticillata and sediment samples were collected in October 1991 from Piscataway Bay and Greenway Flats. *Hydrilla verticillata* was collected from the same sites in July 1992. The plant samples were collected with a rake and wrapped in aluminum foil. The top 5 cm of bed sediment within the *Hydrilla verticillata* beds was collected using a sediment corer and the sediment placed in baked amber glass bottles with Teflon lined caps. All samples were stored in an ice filled cooler until placed in a freezer at -20 °C.

Samples were lyophilized in a freeze dryer with a 2-propanol/dry ice slush trap to prevent back flushing of rough pump oil vapors. Lyophilized sediment samples were stored in a freezer at -20 °C after removing snails and other foreign material from samples. The dried plant material was homogenized in a stainless steel blender, placed in baked amber glass bottles with Teflon lined caps, and stored in a freezer at -20 °C until analyzed.

Plant and sediment samples (n>3) were analyzed according to the procedure developed for tissue analysis for the U.S. Geological Survey National Water Quality Assessment program (Shan, 1992). Samples were analyzed for oxychlordane, α-chlordane, α-chlordane, dieldrin, 4,4'-DDT, and the sum of the PCB congeners identified.

**RESULTS AND DISCUSSION**

An average of 90 µg/kg of total PCB’s were found in the Piscataway Bay *Hydrilla verticillata* collected in 1992 and 70 µg/kg in samples collected in 1991 (fig. 2). Greenway Flats *Hydrilla verticillata* accumulated less than Piscataway Bay with 66 µg/kg and 57 µg/kg total PCB’s in 1992 and 1991, respectively. Piscataway Bay sediment accumulated 83 µg/kg total PCB’s -- 13 µg/kg more than *Hydrilla verticillata* from the same site in 1991, but less than *Hydrilla verticillata* from 1992. The concentrations were higher in the Piscataway Bay sediments than in the Greenway Flats sediments, which contained 23 µg/kg total PCB’s.

*Hydrilla verticillata* from Piscataway Bay in 1991 and 1992 accumulated as much as 10 µg/kg of the chlorinated pesticides measured if DDT is excluded from consideration (fig. 3). Greenway Flats plant concentrations were 7.0 µg/kg and 5.3 µg/kg for 1992 and 1991, respectively. Piscataway Bay sediment contained 6.2 µg/kg, less than the 1991 and 1992 *Hydrilla verticillata* measurements from the same site. Sediment samples from Greenway Flats contained 1.5 µg/kg, the lowest concentration of chlorinated pesticides in this study.

DDT was difficult to quantify, perhaps because of thermal decomposition and (or) affinity with active sites in the gas chromatographic system where DDT can degrade (Bill Foreman, National Water Quality Laboratory, U.S. Geological Survey, oral commun., 1993). Concentration of DDT should be viewed with this in mind.

**Figure 2.** Total PCB concentrations for *Hydrilla verticillata* and sediment samples collected at Piscataway Bay and Greenway Flats, Potomac River, Washington, D.C., October 1991 and July 1992.
In 1990, areal coverage of submerged aquatic plants in the freshwater tidal Potomac River was estimated at 1,652 hectares (Nancy Rybicki, U.S. Geological Survey, oral commun., 1993). A calculation of the mass of PCB's accumulated in submerged aquatic plants in 1990 can be made by using the mean biomass of plants (180 g/m²) for the calendar year 1984 (Carter and Rybicki, 1986). If plant material accumulates as much as 71 μg/kg of total PCB's, the average of the four Hydrilla verticillata sample sets, then about 0.21 kg of total PCB's could be transported from the tidal Potomac River each year during autumn senescence.

CONCLUSIONS

The results of this study demonstrate that Hydrilla verticillata in the tidal Potomac River is accumulating PCBs and chlorinated pesticides.

Accumulation of pesticides and PCBs in Hydrilla verticillata is a significant factor in the redistribution of organochlorine contaminants in the tidal Potomac River.

Autumn senescence and transport downstream of the released leaf material is an important means of bulk transport from the tidal Potomac River towards the Chesapeake Bay.

REFERENCES


Pathways of Methanogenic Biodegradation of Creosote-Derived Aromatic Compounds

By E. Michael Godsy\textsuperscript{1}, Donald F. Goerlitz\textsuperscript{1}, and Dunja Grbic-\textsuperscript{2}Galic\textsuperscript{2}

Abstract

The fate of organic compounds in ground water is controlled by various transport and biotransformation processes. Possibility the most important, but currently the least understood, process affecting ground-water quality is biotransformation of organic compounds by indigenous microorganisms. In this study, the degradation pathways of benzothiophene, quinoline, and naphthalene are determined on the basis of intermediate compounds that appear before and just after the onset of methanogenesis. This study revealed that the biodegradation process consists of both a major and a minor pathway. The first transformation step of the major-pathway heterocyclic compounds is oxidation and cleavage of the heterocyclic ring. After cleavage of this ring, the substituent side chains and the remaining homocyclic ring are subjected to various reactions, including oxidation, decarboxylation, desulfurylation or ammonification, and O-methylation. These reactions are followed by the reduction of the homocyclic ring, cleavage of this ring, \( \beta \)-oxidation, and mineralization. The major pathway intersects both the benzoic acid and phenol methanogenic-degradation pathways. A minor pathway for heterocyclic compounds starting with the oxidation of the homocyclic ring with subsequent ring reduction, ring cleavage, degradation of the remaining heterocyclic ring, and mineralization also was observed.

INTRODUCTION

The fate of homocyclic and heterocyclic aromatic compounds present in creosote and commonly found in subsurface environments is controlled by various transport and biotransformation processes. The most important, but one of the least understood processes affecting ground-water quality, is biotransformation of these contaminants by indigenous microorganisms. Even less is known about these transformations under methanogenic conditions. Several homocyclic and heterocyclic aromatic hydrocarbons, which contain nitrogen and sulfur in their ring structure, have been shown to be susceptible to transformations under methanogenic conditions (Pereira and others, 1987) and to be biodegradable to methane (\( \text{CH}_4 \)) and carbon dioxide (\( \text{CO}_2 \)) (Berry and others, 1987a; Godsy and others, 1989; Godsy and Grbic-\textsuperscript{2}Galic, 1989); the current knowledge has been summarized in four recent review papers (Berry and others, 1987a; Grbic-\textsuperscript{2}Galic, 1989; Grbic-\textsuperscript{2}Galic, 1990; Schink and others, 1992). In this paper, the methanogenic pathways of biodegradation for benzothiophene, indole, quinoline, indene, and naphthalene are investigated. The biodegradation pathways for benzothiophene, quinoline, and naphthalene are inferred from the analysis of intermediate compounds that appear in the growth liquor at the onset and during methanogenesis in laboratory microcosms and from compounds appearing in ground-water samples. No intermediates were detected during methanogenesis of indole and indene except for the end products \( \text{CH}_4 \) and \( \text{CO}_2 \).

MATERIALS AND METHODS

Sample Site

The study site is located adjacent to an abandoned wood-preservation plant within the city limits of Pensacola, Florida (Godsy and others, 1992). The wood-preservation process consisted of steam-pressure treatment of pine poles with creosote or pentachlorophenol (PCP). For more than 80 years, large but unknown quantities of wastewaters consisting of extracted moisture from the poles, cellular debris, creosote, PCP, and diesel fuel from the treatment processes were discharged to nearby surface impoundments. These impoundments were unlined and in direct hydraulic contact with the sand-and-gravel
aquifer. Contamination of the ground water resulted from the accretion of wastes from these impoundments (Mattraw and Franks, 1986).

**Laboratory Microcosms**

Large methanogenic microcosms were constructed in an anaerobic glove box containing a 10 percent hydrogen (H\textsubscript{2})-90 percent argon (Ar) atmosphere. The microcosms were prepared in 4-L glass bottles containing approximately 4 kg of contaminated aquifer material collected at the site near the centroid of the contamination. Microcosms were filled with 2.5 L of anaerobic mineral salts solution composed of the following (per liter): \( \text{KH}_2\text{PO}_4 \), 0.75 g; \( \text{K}_2\text{HPO}_4 \), 0.89 g; \( \text{MgCl}_2\cdot6 \text{H}_2\text{O} \), 0.36 g; \( \text{NH}_4\text{Cl} \), 0.9 g; trace-metal solution (Zeikus, 1977), 9.0 mL; vitamin solution (Wolin and others, 1963), 5.0 mL. The pH was adjusted to 6.0, and the medium was then boiled, cooled and dispensed under a stream of oxygen (O\textsubscript{2})-free Ar gas. The medium was then sterilized at 121 °C for 15 minutes. Control microcosms for each of the tested compounds were autoclaved for 45 minutes and used as killed-cell controls. A positive control was prepared using only the contaminated aquifer material and 2.5 L of anaerobically prepared mineral-salts solution to determine if organic material potentially sorbed onto the aquifer material was biodegradable under the aquifer conditions. One mL/L of sterile amorphous ferrous sulfide (FeS) was aseptically added to all microcosms as a reducing agent (Brock and O'Dea, 1977).

Microcosms were sampled every 1 to 2 days and analyzed by gas chromatography/mass spectrometry (GC/MS) and by high-performance liquid chromatography for intermediates as described by Godsy and Grbic'-Galic' (1989). Only those compounds that appeared in viable microcosms, but not in either control, are reported as intermediates. Ground-water samples were analyzed for possible intermediate compounds by GC/MS as described by Godsy and others (1992). The presence of CH\textsubscript{4} and CO\textsubscript{2} in the microcosms was confirmed by the gas-chromatographic head-space method described by Godsy and others (1992).

**RESULTS**

**Degradation Pathway for Sulfur-Heterocycles**

Compounds detected in the growth liquor just before the onset and during methanogenesis of benzothiophene are shown in figure 1. Compounds that were found in the autoclaved and organic free controls are not shown and presumably do not arise from the degradation of the previously mentioned compounds. More than 33 intermediate compounds were detected in the growth liquor during degradation of this compound. On the basis of the study by Pereira and others (1988), who demonstrated that the first step in the oxidation of quinoline consisted of oxidation of the heterocyclic ring, the sulfur (S)-heterocyclic ring may be oxidized to 2-benzo thiophenone or the tautomer benzo thiophene-2-ol. However, this compound was not detected in the microcosms or in ground-water samples. After hydrolytic cleavage of this ring, the substituent side chains and remaining homocyclic rings were possibly subjected to various reactions including oxidation, decarboxylation, desulfurylation, and O-methylation with ultimate conversion to benzoic acid and phenol. These reactions were most likely followed by the previously described pathways (Berry and others, 1987a) consisting of the reduction of the homocyclic ring, corroborated by the appearance of cyclohexyl alcohol and cyclohexanecarboxylic acid, cleavage of this ring, \( \beta \)-oxidation, and mineralization to CH\textsubscript{4}, CO\textsubscript{2}, and hydrogen sulfide (H\textsubscript{2}S). A minor pathway, based on relative abundance of intermediates of benzothiophene, was observed that started with the oxidation of the homocyclic ring. The first implied intermediate compound was not observed in the microcosms but has been found in ground-water samples. This reaction is presumably followed by the hydrolytic cleavage of the homocyclic ring to thiophene-2-ol. Aliphatic sulfur-containing intermediates of the thiophene-2-ol transformation were also detected in the growth medium, indicating further degradation of the remaining S-heterocyclic ring, and mineralization.

**Degradation Pathway for Nitrogen-Heterocyclic Compounds**

Compounds detected in the growth liquor just before the onset and during methanogenesis of quinoline are shown in figure 2. Pereira and others (1988) demonstrated that the first step in the oxidation of quinoline consisted of oxidation of the heterocyclic ring; the major pathway involves the hydrolytic cleavage of the oxidized ring. The transient appearance of aniline in the growth liquor could indicate that this compound is involved in the major pathway. The minor homocyclic-ring-oxidation pathway observed during the methanogenesis of benzothiophene also was possibly occurring during the methanogenesis of quinoline. The oxidized
Figure 1. Proposed pathways of benzothiophene transformation under methanogenic conditions in aquifer-derived microcosms. All intermediates shown were detected in the culture fluid except for those marked by asterisks.
intermediate of the minor pathway, 8-quinolinone ↔ quinoline-8-ol, was not detected in the microcosms but was found in many of the ground-water samples from the study site. After hydrolytic cleavage of the oxidized homocyclic ring, the remaining compounds were probably subjected to similar reactions that were observed during methanogenesis of benzothiophene. This was corroborated by the appearance of 2,3-dimethylpyridine. The minor pathway was proposed on the basis of the breakdown products that were identified for benzothiophene; however, other than 2,3-dimethylpyridine, no other nitrogen-containing aliphatic intermediates were identified for quinoline in the microcosms. Notably, 2,3-dimethylpyridine did not persist in the microcosms and does not persist during down-gradient travel in the aquifer at the study site and is believed to be mineralized to CH$_4$ and CO$_2$.

During the methanogenesis of indole in the microcosms, oxindole was the only intermediate that was observed before complete conversion to CH$_4$ and CO$_2$. Isatin and anthranilic acid, however, were detected in ground-water samples from the research site. These compounds have been shown to be intermediates in the degradation of indole under denitrifying and, presumably, methanogenic conditions (Madsen and Bollag, 1989).
Ground-water samples from the site contained both 1-naphthalenol and 2-naphthalenol, possible candidates for the first oxidation step for naphthalene. It is not certain at this time whether these particular compounds arose from the degradation of naphthalene or came from creosote itself.

Benzofuran was also observed in the growth medium of naphthalene, but the role of this compound is inconclusive from these studies. This compound, however, probably resulted from a reaction involving the hydroxy-group of 2-hydroxyphenylacetaldehyde (an oxidation intermediate of 2-ethylphenol) and the carbonyl carbon of the aldehyde group, followed by dehydration to yield a furan as proposed by Grbic'-Galic' (1989).

**DISCUSSION AND CONCLUSIONS**

Environmental contamination by homocyclic and heterocyclic aromatic hydrocarbon compounds is widespread; however, little information is available on the biotransformation pathways of this class of compounds under methanogenic conditions and even less on the environmental fate of these compounds in contaminated ground water. In general, recent studies on the methanogenic transformation of aromatic compounds have demonstrated that three major-ring-cleavage transformation pathways are used (Young, 1984; Berry and others, 1987a; Evans and Fuchs, 1988; Schink and others, 1992): (1) the benzoic acid, (2) the resorcinol, and (3) the phloroglucinol pathways. In older reviews, pathways for phenol degradation were proposed that proceeded through complete ring saturation to cyclohexanol, conversion to cyclohexanone, and subsequent ring cleavage (Evans, 1977; Young, 1984). These pathways were based on simple analogy to the benzoate pathway; however, no experimental evidence of their existence has ever been found. An alternative pathway for phenol was postulated through which the quinoid phenol tautomer was reduced to form cyclohexanone. This mechanism takes advantage of the polarizing effect of the hydroxyl group on the \( \pi \)-electron distribution in the aromatic ring (Bakker, 1977; Schink and Tschech, 1988). Recently, evidence has been presented that links the phenol with the benzoate pathway (Knoll and Winter, 1989; Sarak-Genther and others, 1989; Häggblom and others, 1990). The carboxylation of phenol to 4-hydroxybenzoate was proposed as the first step in the degradation. This step was then followed by reduction of the hydroxyl group.

**Degradation Pathway for Homocyclic Compounds**

Intermediate-compound analyses for indene and naphthalene transformation were done in the same manner as for the heterocyclic compounds. The analyses on microcosms containing indene did not reveal any intermediates other than the end products CH\(_4\) and CO\(_2\). The microbes in the aquifer sediments used as the inoculum were presumably very active toward this compound.

The analyses for intermediate compounds of naphthalene (fig. 3) revealed 2-ethylphenol, a compound that would be in the major degradation pathway resulting from the hydrolytic cleavage of one of the naphthalene rings. This intermediate would subsequently be subjected to various reactions similar to the above, resulting in CH\(_4\) and CO\(_2\) as the end products.
and removal to form benzoate. Because the ground-water consortia used for this part of the study were mixed ground-water cultures, it is not surprising that the major transformation pathways for benzothiophene and quinoline intersected segments of both the benzoate or the phenol pathway. It is not known at this point whether phenol or benzoate is more important as the key intermediate in the methanogenic transformation of quinoline and benzothiophene in these microcosms; however, Grbic'-Galic' (1989) found that phenol was the most persistent simple aromatic intermediate of the methanogenic degradation of naphthalene in a fed-batch reactor. It is also not known at this time whether phenol was then degraded by the pathway suggested by Schink and Tschech (1988) or by carboxylation to 4-hydroxybenzoate and then degradation via the benzoate pathway.

The major pathways for anaerobic transformation of benzothiophene and quinoline seem to be initiated by the oxidation and then cleavage of the nitrogen N- or S-heterocyclic ring. Delocalization of the π-electrons in the heterocyclic ring results in the heteroatom being relatively electron depleted and the carbons in the ring being relatively electron enriched. The carbon atom proximal to the heteroatom, as a result of the electron delocalization, is then available to nucleophilic attack by water. This observation is in line with the findings of Berry and others (1987b), who demonstrated that the first step in the methanogenic transformation of indole, the nitrogen analog of benzothiophene, was the oxidation of the N-heterocyclic ring to form oxindole. Similarly, Pereira and others (1988) were able to demonstrate the oxidation of the N-heterocyclic ring of quinoline using $\text{H}_2^{18}\text{O}$ to form $^{18}\text{O}$-labeled 2(1H)-quinolinone under methanogenic conditions; however, they were not able to demonstrate methanogenic fermentation of this compound, probably due to their use of reasonably fresh sewage sludge as the inoculum for the microcosms. In this work, it was found that the substituent side chains attached to the homocyclic ring after the cleavage of the heterocyclic ring were subjected to various transformation reactions, as exemplified by the myriad of single-ring compounds found. The large number of compounds is, undoubtedly, a result of the activity of a complex ground-water consortium.

The other, as yet unreported minor pathway for heterocycles involves the initial oxidation of the homocyclic ring, hydrolytic cleavage of this ring, and then attack on the heterocyclic ring. Several years ago, Vogel and Grbic'-Galic' (1986) showed that the oxidation of an unsubstituted homocyclic aromatic ring was possible when they demonstrated the oxidation of benzene to $\text{CH}_4$ and $\text{CO}_2$ by a mixed methanogenic culture. The magnitude, importance, and organisms involved in the minor transformation pathway for benzothiophene, quinoline, and other creosote-derived compounds are unknown at this time; however, the mechanism and organisms involved in the minor pathway might be similar to those initiating the attack on indene, naphthalene, benzene, and toluene. The oxidation of the homocyclic ring at positions 5 or 8 for quinoline, or at positions 4 or 7 for benzothiophene, are consistent with observations of organic synthesis reactions, where the carbons of the homocyclic ring proximal to the heterocyclic ring are most susceptible to attack (Vollhardt, 1987).

The inability to identify intermediate compounds during the methanogenesis for some compounds (for example, benzofuran and indene) may be because of low initial concentrations of the compounds in the microcosms. Compounds that could be intermediates of these were observed in ground-water samples. 3(2H)-benzofuranone and both 2,3-dihydro-indene-1-one and 1,3-dihydro-indene-2-one were observed in ground-water samples and could be intermediates in the degradation of benzofuran and indene, respectively.

REFERENCES CITED


Modeling Steady-State Methanogenic Degradation of Phenols in Ground Water at Pensacola, Florida

By Barbara A. Bekins¹, E. Michael Godsy¹, and Donald F. Goerlitz¹

Abstract

Field and microcosm observations of methanogenic phenolic-compound degradation indicate that Monod kinetics theory governs the substrate disappearance but overestimates the observed biomass. In this paper, we present modeling results from an ongoing multidisciplinary study of methanogenic biodegradation of phenolic compounds in a sand and gravel aquifer at Pensacola, Florida. The aquifer is contaminated with chemicals and wastes used in wood treatment. Field-disappearance rates of four phenols match those determined in batch microcosm studies performed by other workers in a related study. The degradation process appears to be at steady state because the transported contaminants still are disappearing within 150 meters downgradient of the source even after a sustained influx over several decades. The existence of a steady-state degradation profile of each substrate together with a low bacteria density in the aquifer indicate that the bacterial population is exhibiting no net growth. This is possibly because of the oligotrophic nature of the biomass population in which growth and utilization are approximately independent of the phenolic-compound concentration for most of the concentration range. Thus, a constant bacteria growth rate should exist over much of the contaminated area, which may, in turn, be balanced by an unusually high decay or maintenance rate caused by hostile conditions or predation.

INTRODUCTION

The fate of toxics in anaerobic environments has potential applications to many ground-water contamination problems. Use of unlined wastewater-disposal ponds at a former wood-treatment facility in Pensacola, Fla., led to contamination of a shallow sand and gravel aquifer by creosote, PCP, and diesel fuel (Goerlitz and others, 1985). A native methanogenic-bacteria population has adapted to a sustained influx of the water-soluble fraction of these contaminants (Godsy and others, 1992b) such that the saturated zone has reached an apparent steady-state condition. The dissolved contaminants enter at a constant rate and are degraded within a fixed distance downgradient in the ground-water flow field.

Previous studies of continuous sources have obtained different results. Kindred and Celia (1989) did a theoretical study of one-dimensional solute transport in which the solute reaction rate and associated bacterial growth were described by Monod kinetics. Their results predict an unbounded increase in the mass of bacteria (biomass) near a steady supply of substrate unless the model is altered to include diffusion limitations caused by build-up of a thick biofilm. In addition, unbounded growth in response to continuous substrate supply has been observed as clogging around well bores in wastewater-injection experiments (Ehrlich and others, 1979). In contrast, at the Pensacola site, the volume of bacteria, as determined by Acridine Orange Direct Counts (AODC), is still less than 0.003 percent of the pore space (Godsy and others, 1992b), even though there has been a continuous influx of substrate for decades. Rittman and McCarty (1980) have shown that a steady-state substrate profile can be maintained with a biofilm in an aerobic-column reactor. However, in their study, mass transport internal to the biofilm was an important

rate control, whereas the density of bacteria is much too low for biofilm limitations at the Pensacola site.

The objectives of this paper are to (1) verify that the disappearance rate of phenols at the field site can be modeled using Monod kinetics parameters determined from microcosm studies by Godsy and others (1992a), and (2) formulate a model for steady-state disappearance of a constant influx of contaminants. We concentrate on the fate of four dissolved phenolic compounds: phenol, and 2-, 3-, and 4-methylphenol.

SITE DESCRIPTION

The study site is an abandoned wood-treatment facility in the extreme western end of the Florida Panhandle within the city of Pensacola (fig. 1). For

Figure 1. Location of the abandoned creosote works, test sites, and selected drainage features.
about 80 years, contaminants from unlined waste-disposal ponds entered the ground water in the sand and gravel aquifer.

The aquifer consists of approximately 90 m of poorly sorted fine to coarse-grained deltaic sand deposits interrupted by discontinuous silts and clays (Franks, 1988). The water table is about 1.5 m below the land surface. A generalized geologic section through the study area is shown in figure 2. The sand deposits have a fairly uniform average porosity of 0.38. A grain-size analysis of a sediment sample from a depth of 6 m at site 39 gave an average grain size of 0.335 mm with a d10 = 0.1 mm and a d60 = 0.5. Sorption of the phenolic compounds is relatively unimportant, because the organic fraction of the aquifer material is only 0.07 percent.

Concentrations of the four phenolic compounds (phenol, and 2-, 3-, and 4-methylphenol) have been monitored at the study site for more than 12 years. The data indicate that the contaminants were undergoing steady-state degradation during this period. Data from 6 m below the surface was chosen for the analysis presented in this paper because this depth is well within the methanogenic part of the contaminated zone; it is below the depth at which recharge and any floating hydrocarbon at the water table affect concentrations; and it is above the clay lenses in a zone where the assumption of one-dimensional flow applies (fig. 2).

**MODEL DESCRIPTION**

Monod kinetics describes the utilization of a single growth-limiting substrate by the bacteria population:

\[
\frac{dS}{dt} = \frac{\mu_m BS}{Y K_s + S}
\]

where \( S \) is the limiting substrate concentration, in milligrams per liter; \( \mu_m \) is the maximum growth rate, in \( \text{day}^{-1} \); \( Y \) is the biomass growth yield, in milligrams biomass per milligram substrate; \( K_s \) is the half-saturation constant, in milligrams per liter; and \( B \) is the biomass concentration, in milligrams per liter (Monod, 1950). We assume that the growth is carbon limited at this site based on inorganic analyses of the pore waters performed by Godsy and others (1992b). Thus, we use the single substrate Monod reaction term given in eq. 1, and in each simulation, a single phenolic compound serves as the sole carbon source.

The resulting growth of biomass due to utilization of the substrate is

\[
\frac{dB}{dt} = \left( \frac{\mu_m S}{K_s + S} - b \right) B
\]

where \( b \) is the biomass specific decay or death rate, in \( \text{day}^{-1} \).

Godsy and others (1992a) established laboratory microcosms simulating the methanogenic conditions in the subsurface environment and determined utilization rates for the four phenolic compounds. They fit the change in concentration with time of each phenol and the associated microbial growth to equations 1 and 2.
using nonlinear regression analysis. Table 1 shows the Monod kinetics constants obtained from the fits for each compound.

We assume that the substrate profile at a depth of 6 m satisfies the one-dimensional, transport equation with a Monod reaction term:

$$\frac{\partial S}{\partial t} = D \frac{\partial^2 S}{\partial x^2} - v \frac{\partial S}{\partial x} - \frac{\mu_m B S}{Y \Theta K_s + S},$$

(3)

where $t$ is time, in days; $x$ is distance downgradient from site 3; $D$ is the dispersion coefficient; $v$ is average linear velocity, in meters per day; $B$ is milligrams of bacteria per liter of sediment; and $\Theta$ is the porosity. A one-dimensional model is appropriate for this site because the flow direction is primarily horizontal and perpendicular to a wide contaminant source. In this initial model, the spatial distribution of biomass, $B$, is uniform. This is consistent with results from Godsy and others (1992b) who found, at a depth of 6 m, a constant density of bacteria within the contaminated zone. Bekins and others (1993) showed that the observed substrate profile cannot exist at steady-state if the bacteria concentration is changing with time. Therefore, the model biomass value also does not change with time.

Equation 3 was solved numerically using a computer code developed by Kindred and Celia (1989). The boundary conditions used were

$$S(\phi, t) = S_\phi, \quad \left. \frac{\partial S}{\partial x} \right|_{x = 250} = 0,$$

(4)

where $S_\phi$ is the contaminant concentration 6 m below the ground surface at site 3, the closest site to the source. The initial condition used was

$$S(x, \phi) = S_\phi,$$

(5)

RESULTS AND DISCUSSION

Results of simulations indicate that the concentrations of phenolic compounds at the field site will reach steady-state profiles within 1,000 days. Two predicted substrate profiles, after 1,000 days along with measured phenolic-compound concentrations of Goerlitz (1992) at 6 m below land surface at each site are shown in figure 3A. The measured data values are from sites 3, 39, 40, 4, and 37, from left to right, respectively. The computed profiles are steady-state solutions to a one-dimensional advective-dispersive equation with a biological reaction term (eq. 3). Biomass is held constant during the simulation. The upper curve predicts the field profile that would result from the phenol degradation rate that was measured in the lab, whereas the lower one corresponds to the rate measured for 2-methylphenol. These two rates were used because they have the smallest associated errors and bracket the rates for the other two compounds (table 1). The parameters used in the solution for phenol and 3-methylphenol were: $S_\phi = 26.0$, $\mu_m = 0.111 d^{-1}$, $Y = 0.013$, $K_s = 1.33 \text{ mg/L}$, $B = 1.5 \times 10^{-2} \text{ mg/L}$, $v = 1.0 \text{ m/d}$, $D = 1.0 \text{ m}^2/d$. For 2- and 4- methylphenol, the values used were: $S_\phi = 13.5 \text{ mg/L}$, $\mu_m = 0.044 d^{-1}$, $Y = 0.022$, $K_s = 0.25 \text{ mg/L}$, $B = 3.0 \times 10^{-2} \text{ mg/L}$, $v = 1.0 \text{ m/d}$, $D = 1.0 \text{ m}^2/d$.

The model profiles indicate that the microcosm simulations accurately represent the degradation process taking place in the field. The validity of the Monod kinetics expression for the degradation rate is apparent from the field data because the rate of decrease in the phenol concentration changes dramatically around site 40 (located about 90 m downgradient from site 3). When the substrate concentration is high (upgradient of site 40), the degradation kinetics can be approximated by a zero-

---

Table 1. Kinetic constants for microcosm studies for each of the compounds tested with ± 95 percent confidence intervals.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\mu_m$ (d$^{-1}$)</th>
<th>$K_s$ (mg/L)</th>
<th>$b$ (d$^{-1}$)</th>
<th>$Y$ (mg/mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol</td>
<td>.111±.005</td>
<td>1.33±.07</td>
<td>.001±.012</td>
<td>.013</td>
</tr>
<tr>
<td>2-Methylphenol</td>
<td>.044±.001</td>
<td>.25±.82</td>
<td>.002±.008</td>
<td>.022</td>
</tr>
<tr>
<td>3-Methylphenol</td>
<td>.103±.078</td>
<td>.55±.67</td>
<td>.000±.019</td>
<td>.026</td>
</tr>
<tr>
<td>4-Methylphenol</td>
<td>.099±.110</td>
<td>3.34±11.1</td>
<td>.000±.032</td>
<td>.025</td>
</tr>
</tbody>
</table>

$^1Y$ values obtained from protein determinations before and after substrate utilization.
order reaction term consistent with the low values of $K_s$ observed in the lab studies. When the substrate concentration is close to the value of $K_s$, the degradation rate drops as predicted by Monod kinetics. Thus, modeling confirms that the degradation rate is accurately described by Monod kinetics.

The biomass concentration used for each model profile was obtained by performing a least-squares fit of the computed concentration to the measured field data. The two values of $B$ obtained using this method are: $1.5 \times 10^{-2}$ mg/L for the steeper profile and $3.0 \times 10^{-2}$ mg/L for the lower profile (or, in terms of numbers of bacteria per 100 g sediment, $4.8 \times 10^6$ and $9.6 \times 10^6$ respectively). An important point is that these numbers represent estimates of only the active bacteria mass controlling the rate-limiting step in the entire degradation process.

The fitted biomass estimates can be compared to the value measured in sediments from a 6-m depth at site 39 (located 65 m downgradient from site 3). This was determined from analyses of total proteins in 10 g subsamples of the aquifer material by modification of the method of Bradford (1976) as described by Galli (1987). The total biomass concentration was $1.3 \pm 0.07 \times 10^2$ mg/L. Recall that the fitted value represents only the mass of active bacteria in the limiting step of the degradation process. Godsy and others (1992b) suggest that methanogenesis is the limiting step based on an observed build-up of acetate both in the microcosms and in the field. They determined that the methanogenic bacteria account for only 0.1 percent of the total bacteria population. Moreover, their Most Probable Number estimates of the mass of active bacteria were about 10 percent of the total biomass determined by AODC. Combining these results indicates that the active methanogenic biomass should be about four orders of magnitude less than the value obtained from total protein analyses, or $1.3 \pm 0.07 \times 10^{-2}$ mg/L. This agrees well with our fitted estimates of $1.5 - 3.0 \times 10^{-2}$ mg/L.

The most interesting result arising from the modeling is the evidence that the growth of bacteria within the contaminated region is independent of the substrate concentration and that the net growth is zero. The theoretical single compound growth rates corresponding to the model substrate profiles are shown in figure 3B. These growth rates were computed from eq. 2 with the parameters in table 1 and a decay value, $b$, of zero. In the first 65 m, the growth rates are nearly independent of the substrate concentration. This is a consequence of the very low half-saturation values, $K_s$, typical of the oligotrophic populations found in aquifers. This nearly constant growth rate may be balanced by a standard zero-order decay term ($b$ in eq. 2) to achieve zero net growth. However, beyond 65 m, the predicted growth rates on phenol and 3-methylphenol drop off, and beyond 90 m, the growth rates on 2- and 4-methylphenol also decrease.

Possibly, as the growth rate on the phenolic compounds begins to decrease, other compounds then serve as substrates. Candidates for this are oxindole and quinolinone. These compounds are oxidized intermediates of indole and quinoline. They appear after 20 to 30 days in microcosm studies and are found at site 3 in the field (Godsy, 1993). They are energetically favorable to growth with Monod growth.
Figure 4. (A) Computed concentration profile for phenol that includes inhibition effects from the total phenol concentration shown together with measured concentration and the Monod growth expression with and without the modification for Haldane inhibition.

The decay or maintenance rate required to balance the predicted growth rate is unusually high. Suidan and others (1989) give a value of 0.0192 day$^{-1}$ for a continuous-reactor study whereas Godsy and others (1992a) obtained a value of approximately 0.001 day$^{-1}$ on the basis of microcosm studies. These values are too low to balance the 0.04-0.1 day$^{-1}$ growth rates shown in fig. 3B.

Inhibition of growth by various compounds was considered to be a possible explanation of the low bacteria population. Total phenolic-compound concentrations exceed 100 mg/L upgradient from site 3 and are, thus, high enough to slow degradation and growth by about 20 percent (Suidan and others, 1989). Substrate inhibition may be modeled by modifying the biological reaction term in equation 3 according to the Haldane inhibition model (Haldane, 1930):

$$\frac{\partial S}{\partial t} = \frac{D}{\partial x^2} - \frac{\mu_m B}{Y \Theta \left( \frac{S}{K_s + S + \left( \frac{S}{T} \right)^2}/K_i \right)}$$

where $S_T$ is the total phenol concentration and $K_i$ is the Haldane inhibition constant (in mg/L).

A computed steady-state solution to eq. 6 for phenol using a value for $K_i$ obtained by Suidan and others (1989) of 363 mg/L is shown in fig. 4A. The value of $B$ that best fit the data is $2.4 \times 10^{-2}$ mg/L. The remaining model parameters are the same as used for fig. 3. The expected biomass growth rate on phenol under the Haldane model is shown in figure 4B. For comparison, the growth rate for phenol with no inhibition is also shown. The inhibited growth rate is significantly lower than the growth rate predicted by the model with no inhibition; however, it is still higher than the decay rate in Suidan and others (1989).

CONCLUSIONS

In summary, we have shown that Monod degradation constants measured in simulated methanogenic ecosystems accurately describe phenolic-compound degradation rates observed in the sand and gravel aquifer at the study site. In order to describe the natural system however, the model requires that there be no net growth in the aquifer biomass. This constraint is consistent with the field data because the biomass concentration in the aquifer is relatively low in spite of the continuous influx of substrate over many decades. The explanation for the constant biomass concentration may involve a combination of two factors: First, the oligotrophic population exhibits growth that is independent of the...
substrate concentration near the contaminant source. Second, where the growth rate begins to decline as the phenolic-compound concentrations approach the half-saturation constants, the biomass may begin to consume other substrates. These may be organic compounds from lysed cells upgradient, or other contaminants that appear to persist for a longer time than the phenolic compounds but allow similar bacterial growth rates. Finally, a high decay rate is required to balance the proposed constant bacterial growth rate. This may be due to the hostility of the environment, transport of cells downgradient, or predation by other organisms.

REFERENCES


Abstract

Laboratory-column breakthrough curves for the nitrogen-containing heterocyclic compounds found in the water soluble fraction of creosote were modeled and compared assuming local equilibrium and nonequilibrium conditions. The aquifer material consisted of a low organic-carbon-content (0.024 percent organic carbon), low ion-exchange-capacity (2 meq/100 g) clayey sand. Retardation factors and partition coefficients for quinoline, 2(H)-quinolinone, carbazole, and acridine, derived from breakthrough curves, were contrasted with those obtained from batch experiments. Retardation factors for quinoline and 2(H)-quinolinone were comparable to each other, although those for carbazole and acridine were quite different despite similar chemical structures and octanol-water partition coefficients. Transport of quinoline, 2(H)-quinolinone, and acridine is governed by organic and ionic interactions; however, transport of carbazole is controlled by organic interactions alone. In addition, although the local equilibrium assumption can be used to describe quinoline and 2(H)-quinolinone breakthrough curves, carbazole and acridine breakthrough curves require nonequilibrium kinetics.

INTRODUCTION

Modeling is necessary to predict the fate and transport of organic contaminants in aquifers. Model parameters must be estimated or determined either from field studies or laboratory experiments. Commonly, model input data are generated from properties of water that are not comparable to the properties of ground water at the site of contamination. Ground-water characteristics, such as pH, must be compared to ionization constants (pKₐ) to determine the effects of the sediment's ion exchange capacity. Simulated transport will not be accurate if the parameter at a pH differs from that of the ground water. In addition, laboratory studies commonly yield values for parameters using methods that do not reflect field conditions. For example, batch or column studies are used to determine partition coefficients, even though batch studies, often performed without considering the rate at which equilibrium is approached, do not consider nonequilibrium partitioning between aqueous and solid phases and column studies do not necessarily use representative packing or ground-water velocities.

In this paper, we compare the values of partition coefficients and retardation factors for quinoline, 2(H)-quinolinone, carbazole, and acridine by two different laboratory methods on low organic-carbon-content, low ion-exchange capacity aquifer material. The partition coefficients and retardation factors vary with the measurement method, most notably for acridine. In addition, we compare the results obtained for different equilibrium assumptions used in modeling column effluent. Column effluents were modeled successfully using the local equilibrium assumption for quinoline and 2(H)-quinolinone and the nonequilibrium assumption for carbazole and acridine. Column studies are preferred over equilibrium batch studies because column studies yield more data under conditions similar to those in the field. However, to determine sorption rate constants independently, batch experiments measuring the rate at which equilibrium is attained must be conducted in conjunction with column experiments (Ball and Roberts, 1991b).
Site description

The study-site aquifer consists of quartz sand and gravel with interspersed silt and clay lenses (Franks, 1988). During 1902-81, wood-treatment wastes were discarded into impoundments that were in direct contact with the ground water. Creosote and pentachlorophenol wastes migrated vertically into the subsurface. The ground water, at a pH of approximately 5.9 and moving at a speed of about 1 m/d, continually dissolved the more soluble compounds in creosote creating an extended water soluble fraction (WSF) contamination plume. A major fraction of the WSF consists of the nitrogen heterocycles (for example, quinoline, carbazole, and acridine, as well as 2(1H)-quinolinone, a microbial degradation product) (Godsy and others, 1992).

Models

The transport of the WSF in laboratory columns can be described by the convection-dispersion equation using the local equilibrium assumption (LEA) as proposed by Hashimoto and others (1964)--

$$D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} = R \frac{\partial C}{\partial t},$$

where

- $D$ is the dispersion coefficient [m$^2$/d],
- $C$ is aqueous concentration [g/m$^3$],
- $v$ is linear velocity [m/d],
- $x$ is distance [m],
- $t$ is time [d], and
- $R$ relates the movement of a contaminant to a conservative tracer [-].

Equation 1 assumes a linear Freundlich isotherm (Freundlich, 1926):

$$\bar{C} = K_d C,$$

where

- $\bar{C}$ is mass concentration of contaminant adsorbed onto the adsorbent [g/g] and
- $K_d$ relates aqueous concentration to sorbed concentration [m$^3$/g].

Retardation factors, $R$, and partition coefficients, $K_d$, are related by

$$R = 1 + \frac{\rho_b K_d}{\theta},$$

where

- $\rho_b$ is the bulk density of the aquifer material [g/m$^3$] and
- $\theta$ is the porosity [-].

Transport commonly must be modeled using the nonequilibrium assumption (NEA) as proposed by van Genuchten and Wierenga (1976), which accounts for a readily mobile fraction and a stagnant or immobile fraction of water in the aquifer matrix (subscripts $m$ and $im$, respectively)--

$$\left[\theta_m + (1-f) \rho_b K_d \right] \frac{\partial C_m}{\partial t} + \left[\theta_m + (1-f) \frac{\rho_m}{\rho_b} K_d \right] \frac{\partial C_m}{\partial x} = \theta_m D \frac{\partial^2 C_m}{\partial x^2} - v_m \theta_m \frac{\partial C_m}{\partial x}$$

$$\left[\theta_{im} + (1-f) \rho_b K_d \right] \frac{\partial C_{im}}{\partial t} = \alpha_1 (C_m - C_{im}).$$

where

- $f$ is the fraction of sorption sites in the mobile region [ - ] and
- $\alpha_1$ defines the transfer rate of the solute between mobile and immobile water [d$^{-1}$].

The model is based on the assumption that convection and dispersion govern transport in the mobile water and diffusion controls the transfer of contaminant between mobile and immobile water. The model includes two fitted dimensionless parameters: $\omega$, the ratio of hydrodynamic residence time to characteristic time of sorption (Brusseau and Reid, 1991); and $\beta$, the relative contribution of the sites accessible to mobile water to the overall retardation. The original coefficients, $\alpha_1$ and $f$, relate to $\omega$ and $\beta$ as follows:

$$f = \beta + \frac{\theta \beta - \theta_m}{\rho_b K_d}$$

$$\alpha_1 = \frac{\omega q}{L}.$$
Organic-carbon content of the aquifer material was measured by the Walkley-Black Method (Walkley and Black, 1934) as described in Methods of Soil Analysis (Black and others, 1965, p. 1372). Cation-exchange capacity of the aquifer material was determined by the method of Black and others (1965, p. 899) using ion chromatography.

Aqueous samples were analyzed for organic compounds by reverse phase high-performance liquid chromatography (HPLC) using gradient elution of 5 to 100 percent acetonitrile in 26 mM ammonium acetate, pH 7.6 on a C-18 column with a diode-array detector.

The batch studies involved five different concentrations (table 2), in duplicate, of quinoline, 2(1H)-quinolinone, and acridine in 15 mM CaCl₂ (pH 5.9), sterilized through a filter with a 0.45-μm pore size, and added to autoclaved 10 mL serum bottles with and without aquifer material. The serum bottles were sealed with Teflon-lined butyl rubber septa and aluminum crimp seals. The samples were first shaken rapidly for 2 days at room temperature (23 ± 2°C) and then allowed to equilibrate in the dark at room temperature with intermittent shaking before sampling. Samples were checked for equilibrium conditions by periodically sacrificing bottles of the same concentration. The concentration of the compounds in the bottles with aquifer material was compared to the concentration in the bottles without aquifer material to determine the mass of compound adsorbed onto the aquifer material. Samples were checked for sterility at the end of the experiment. No bacterial contamination was found.

Columns were prepared using dried aquifer material. The aquifer material was first passed through a 1.0 mm sieve, removing less than 0.3 percent by weight. The sediment was dampened slightly to aggregate the material and packed into a glass column, 1 to 3 mm at a time, as described by Goerlitz (1984). The column characteristics are given in table 1. A constant-flow HPLC syringe pump was connected to the influent end of the column and a variable wavelength UV detector and a refractometer were connected to the effluent end. All the fittings and tubing were either glass, stainless steel, or Teflon. All CaCl₂ solutions were degassed and filtered before use. Ten mM CaCl₂ at pH 5.9 was pumped through the column until the column reached equilibrium. The compounds were dissolved into 15 mM CaCl₂ at pH 5.9 and run through the column at approximately 120 × 10⁻⁶ m³/d until the CaCl₂ concentration in the effluent equaled that in the influent (table 2). This flow rate is approximately equal to a linear velocity of 1 m/d in the aquifer.

Parameters-R for the LEA and R, β, and ω for NEA were fit to the breakthrough curves (BTC’s) using nonlinear regression analysis. BTC’s were analyzed by use of the computer program HASHPE (Oravitza, 1984) to determine LEA parameters and the computer program CFITIM (van Genuchten, 1981) to determine NEA parameters. The dispersion parameter for all model simulations was determined from CaCl₂ breakthrough.

### Table 1. Aquifer material and column characteristics

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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<tbody>
<tr>
<td>Median particle diameter [m]</td>
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<td>Percent organic carbon [-]</td>
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<td>Cation exchange capacity [meq/100 g]</td>
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<td>Column</td>
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</tr>
<tr>
<td>Length [m]</td>
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<tr>
<td>Diameter [m]</td>
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<tr>
<td>Porosity [-]</td>
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<tr>
<td>Bulk Density [g/m³ x 10⁻⁶]</td>
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</tr>
<tr>
<td>Flow Rate [m³/d x 10⁻⁶]</td>
<td>140</td>
</tr>
</tbody>
</table>

### Table 2. Concentrations of quinoline, 2(1H)-quinolinone, carbazole, and acridine for batch and column studies

<table>
<thead>
<tr>
<th>Compound</th>
<th>Batch</th>
<th>Column</th>
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</thead>
<tbody>
<tr>
<td>Quinoline</td>
<td>140</td>
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</tr>
<tr>
<td>2(1H)-Quinolinone</td>
<td>53</td>
<td>2.5</td>
</tr>
<tr>
<td>Carbazole</td>
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<td>8.9</td>
</tr>
<tr>
<td>Acridine</td>
<td>19</td>
<td>18</td>
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### RESULTS

#### Batch Studies

Linear Freundlich partition coefficients for batch studies of quinoline, 2(1H)-quinolinone, and acridine were determined by linear regression (with the y-intercept forced to zero) on the aqueous and sorbed concentrations (table 3). The r² values for acridine and 2(1H)-quinolinone were 0.95. The r² value for quinoline was 0.85. This value is low because quinoline exhibited nonlinear sorption, confirming that reported by Zachara and others (1986). Despite this, the local equilibrium model, which is based on the assumption of linearity, closely reproduced quinoline in the column effluent, possibly because of a low selectivity coefficient.
Table 3. \( pK_a \), \( \log K_{ow} \), partition coefficients, and retardation factors for quinoline, 2(1H)-quinolinone, carbazole, and acridine

Partition coefficients in cubic meter per gram \( \times 10^6 \)

<table>
<thead>
<tr>
<th></th>
<th>( pK_a )(^1)</th>
<th>( \log K_{ow} )(^2)</th>
<th>Partition coefficient(^3)</th>
<th>Retardation factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quinoline</td>
<td>4.90</td>
<td>2.03</td>
<td>0.133</td>
<td>1.40</td>
</tr>
<tr>
<td>2(1H)-Quinolinone</td>
<td>5.29</td>
<td>1.26</td>
<td>.231</td>
<td>1.70</td>
</tr>
<tr>
<td>Carbazole</td>
<td>-5.70</td>
<td>3.29</td>
<td>4.56</td>
<td></td>
</tr>
<tr>
<td>Acridine</td>
<td>5.60</td>
<td>3.40</td>
<td>4.56</td>
<td>14.8</td>
</tr>
</tbody>
</table>

\(^2\) (Hansch and Leo, 1979).
\(^3\) Determined using linear regression on the aqueous and sorbed batch concentrations.
\(^4\) Calculated using equation 3.
\(^5\) Determined using local equilibrium assumption for quinoline and 2(1H)-quinolinone and nonequilibrium assumption for carbazole and acridine.

**Column Studies**

Retardation factors for quinoline and 2(1H)-quinolinone were similar (table 3). 2(1H)-Quinolinone, with a \( pK_a \) of 5.29 (table 3), is approximately 20 percent ionized and quinoline, with a \( pK_a \) of 4.9, is approximately 9.1 percent ionized. Zachara and others (1986) have shown that sorption of quinoline is dominated by ion exchange up to 2 pH units above its \( pK_a \). 2(1H)-Quinolinone, like quinoline, should be retained by ion exchange and organic sorption. The retardation of acridine is significantly higher than that of carbazole despite the fact that both have two benzene rings fused to a nitrogen heterocyclic ring (fig. 1) and have similar octanol-water partition coefficients (table 3). However, the \( pK_a \) of acridine is 5.6 and that of carbazole is -5.7 (table 3). Thus, at pH 5.9, the ionized fraction of acridine is 0.33, but carbazole is completely un-ionized. The degree of affinity of acridine to charged functional groups on the aquifer material (the selectivity coefficient) and the extent of ionization as well as the cation-exchange capacity contributes to the exchange capacity. With an acridine concentration of 18 g/m³ (0.10 meq/L), the column capacity due to ion exchange is 160. The column capacity is based on the assumption of total sorption of the ionized fraction of acridine to the aquifer material and complete displacement of calcium ions.

![Chemical structures of quinoline, 2(1H)-quinolinone, carbazole, and acridine.](image)

**Figure 1.** Chemical structures of quinoline, 2(1H)-quinolinone, carbazole, and acridine.
LEA and NEA Models

Breakthrough curves for quinoline, 2(1H)-quinolinone, carbazole, and acridine were modeled using both LEA and NEA. The BTC's for 2(1H)-quinolinone and the conservative tracer, CaCl$_2$, for both LEA and NEA fitted models are shown in figure 2. LEA and NEA models are indistinguishable.

The BTC for acridine along with LEA and NEA fitted models are shown in figure 3. The LEA model does not follow the BTC at any time. Carbazole gave similar results (data not shown). The results indicate that, under flow conditions similar to that at the study site, transport of acridine and carbazole is controlled by nonequilibrium conditions and transport of quinoline and 2(1H)-quinolinone is controlled by equilibrium conditions.

Fitted parameters and original coefficients for quinoline, 2(1H)-quinolinone, carbazole, and acridine using the NEA model are given in table 4. The values of $\beta$ for carbazole and acridine agree with each other.

The value of $\omega$ for carbazole, however, is about twice that for acridine, indicating that the characteristic time of sorption contributes more to acridine transport than to carbazole transport.

DISCUSSION AND CONCLUSION

Transport of nitrogen heterocycles is governed by the retardation and the rate at which equilibrium is approached, both of which must be determined to model transport and sorption processes properly. The values of both parameters used in models depend on ground-water pH, water velocities, and contaminant concentrations, among other factors. To reduce error in the laboratory studies, these variables must be similar to that of the ground water at the contaminated site. The effects of ion exchange can have a profound effect on transport of weakly acidic or basic compounds. Transport under nonequilibrium conditions will also affect initial breakthrough and tailing. Without accurate laboratory-generated data, models may produce erroneous results.
Figure 3. Acridine breakthrough curves from column data and local equilibrium (LEA) and nonequilibrium (NEA) assumption fitted models. Relative concentrations \( C' \) were calculated using \( C - C_0 \), where \( C \) is the effluent concentration, \( C_0 \) is the original concentration at the start of the experiment, and \( C_i \) is the influent concentration. Pore volumes \( [-] \) were determined by dividing time by the time it takes for one-half of the relative concentration of CaCl\(_2\) to move through the column.

Table 4. Nonequilibrium assumption parameter values for quinoline, 2(1H)-quinolinone, carbazole, and acridine

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \beta )</th>
<th>( f_{\text{v}} )</th>
<th>( \omega )</th>
<th>( \alpha_1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quinoline</td>
<td>0.0</td>
<td>0.0</td>
<td>160</td>
<td>110</td>
</tr>
<tr>
<td>2(1H)-Quinolinone</td>
<td>0.0</td>
<td>0.0</td>
<td>1,300</td>
<td>900</td>
</tr>
<tr>
<td>Carbazole</td>
<td>0.60</td>
<td>0.60</td>
<td>2.6</td>
<td>1.8</td>
</tr>
<tr>
<td>Acridine</td>
<td>0.61</td>
<td>0.61</td>
<td>1.2</td>
<td>1.8</td>
</tr>
</tbody>
</table>

1/ Calculated assuming \( \theta - \theta_m \) equals zero (van Genuchten and Wierenga, 1976) in equation 6.
2/ Calculated using equation 7.

In this study, parameter values determined from batch and column studies for quinoline and 2(1H)-quinolinone, compounds with low octanol-water partition coefficients, were similar. However, the two methods gave quite different results for acridine. This is to be expected because equilibrium batch studies give values for LEA parameters and column studies under conditions similar to those in the field give values for NEA parameters. Batch or column studies are often used to generate model parameters. Both types of studies have advantages and disadvantages. Batch experiments have been criticized as (1) using a large liquid to sediment ratio and improperly represented sediment characteristics (Barrow and Shaw, 1975; Sparks, 1985; Ball and Roberts, 1991a; Kookana and others, 1992), and (2) not modeling actual flow-field conditions (Freeze and Cherry, 1979; Ball and Roberts, 1991b). Column experiments commonly are subject to unrealistic flows and packing (Johnson and Farmer, 1993) and cannot determine the specific reason for nonequilibrium transport.

Although retardation factors for quinoline and 2(1H)-quinolinone, both of which are partially ionized, were comparable, those for carbazole and acridine were quite different. This difference indicates that ion exchange plays a large role in the transport of contaminants in the aquifer material. This study shows that transport of quinoline, 2(1H)-quinolinone, and acridine is governed by ionic and organic interactions, but that carbazole is controlled by organic interactions alone.
The LEA model sufficiently describes the column effluent for quinoline and 2(1H)-quinolinone. However, the NEA model must be used for carbazole and acridine. Brusseau and Rao (1989) suggest that, for values of $\omega$ less than 10, the NEA should be used instead of the LEA. The values of $\omega$ for carbazole and acridine are well below the value suggested by Brusseau and Rao, justifying the use of the NEA model. Godsy (1993) observed that NEA provides a better fit to data when the log $K_{ow}$ is greater than 2.5. The specific reason for nonequilibrium-diffusion between mobile and immobile water and (or) the kinetics of sorption to organic or ionic sites-cannot be determined from BTC analysis and must be resolved by rate batch studies. Column models show the importance of nonequilibrium in describing transport of contaminants. Equilibrium batch studies, on the other hand, do not indicate whether a contaminant, under field flow conditions, is actually at equilibrium. This distinction is important when modeling transport in the ground water.

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Bioremediation of Petroleum and Metal Contamination with Dissimilatory Metal Reduction

By Derek R. Lovley

Abstract

The possibility that the metabolism of dissimilatory metal-reducing microorganisms might be used for removing organic contaminants and metals from contaminated environments was investigated. The Fe(III) chelator, nitrilotriacetic acid (NTA) enhanced the degradation of toluene in petroleum-contaminated aquifer material in which Fe(III) reduction was the terminal electron-accepting process. Addition of Fe(III) oxide containing sediments stimulated toluene degradation in sediments that were originally methanogenic. These results suggest that increasing the availability of Fe(III) may be a useful bioremediation strategy in aquifers that are heavily contaminated with aromatic compounds. Studies on the mechanism for U(VI) reduction by Desulfovibrio vulgaris indicated that cytochrome $c_3$ is the U(VI) and Cr(VI) reductase. Cytochrome $c_3$ reduced U(VI) in uranium-contaminated mine drainage and ground water. This finding indicates that it may be possible to genetically engineer microorganisms with enhanced metal-reducing capacity. These studies demonstrate that dissimilatory metal reduction may be a useful mechanism for bioremediating organic and (or) metal contamination in some environments.

INTRODUCTION

The potential for bioremediation of environments contaminated with organic compounds is well known. The goal of bioremediation is to convert toxic organic compounds to nontoxic compound(s), typically carbon dioxide. Most studies on the in situ bioremediation of organic contaminants in ground water have focused on oxidation of organic contaminants coupled to the reduction of oxygen. However, Fe(III) is typically the most abundant electron acceptor available for organic matter oxidation when organic contaminants are introduced into previously pristine shallow aquifers (Lovley, 1991). Previous studies have indicated that Fe(III) reduction is an important intrinsic process that naturally removes organic contaminants from polluted ground water (Lovley and others, 1989; Lyngkilde and Christensen, 1992; Baedecker and others, 1993). Thus, if it were possible to stimulate the activity of Fe(III)-reducing microorganisms in contaminated aquifers, the rate at which organic contaminants were degraded might be enhanced.

In contrast to organic contaminants, metal contaminants are not "biodegradable." However, a number of important contaminant metals are less soluble in the reduced state than they are in the oxidized state (Lovley, 1993b). For example, microbial uranium reduction converts the oxidized soluble form of uranium, U(VI) to U(IV) which precipitates from most natural waters (Lovley and others, 1991). This reductive precipitation can effectively remove uranium from a variety of uranium-contaminated waters (Lovley and Phillips, 1992b) and can be used in conjunction with a soil-extraction technique for concentrating uranium from contaminated soils (Lovley, 1993b). In a similar manner, numerous microorganisms can reduce highly soluble and toxic Cr(VI) to less soluble, less toxic, Cr(III) (Lovley, 1993b).

The purpose of the studies reported here was to further investigations on the potential for using dissimilatory metal reduction as a tool for bioremediating organic and inorganic contaminants.
BIOREMEDIATION OF ORGANIC CONTAMINATION

Studies with the dissimilatory Fe(III)-reducing microorganism *Geobacter metallireducens* (strain GS-15) demonstrated that the reduction of Fe(III) could be greatly stimulated with the metal chelating compound nitrilotriacetic acid (NTA) (data not shown). Thus, the potential for using NTA to stimulate the oxidation of organic contaminants coupled to Fe(III) reduction in ground water was evaluated with aquifer material collected from a petroleum-contaminated aquifer located in Hanahan, S.C. (Vroblesky and Chapelle, 1996). Zones in which Fe(III) reduction or methane production were the terminal electron-accepting processes (TEAPs) were located using measurements of dissolved H₂ and the TEAPs in the sediments were confirmed with laboratory incubations and the use of radiolabeled tracers. Sediments that had been collected by hand augering were incubated under strict anaerobic conditions in serum bottles. Heat-killed controls were generated by autoclaving sediments. Toluene was selected as a typical aromatic ground water pollutant. Toluene and NTA dissolved in oxygen-free water were added to the sediments in order to provide initial concentrations of 10 μM and 4 mM, respectively. Metabolism of toluene over time was monitored by sampling the headspace with a syringe and needle and analyzing the headspace gas for toluene with a gas chromatograph equipped with a flame ionization detector.

There was a steady loss in toluene concentrations over time in sediments from the Fe(III)-reducing zone (fig. 1). If the microorganisms in the sediment were

![Figure 1](image_url)

**Figure 1.** Effect of nitrilotriacetic acid (NTA) on the loss of toluene over time in Fe(III)-reducing sediments. The designation killed indicates that the microorganisms in the sediment were killed with heat prior to the addition of toluene. Toluene was added at an initial concentration of 10 μM and an equivalent amount of toluene was again added to the sediments containing live microorganisms that had been amended with NTA at the times designated by the arrows along the x-axis. Integration units specify the numerical area calculated by an electronic integrator for the size of the toluene peak detected by the gas chromatograph.
Toluene-Methanogenic Sediments
Toluene-Fe(III) Amended Sediments
Methane-Methanogenic Sediments
Methane-Fe(III) Amended Sediments

Figure 2. Effect of addition of Fe(III)-oxide containing sediments to sediments in which methane production was the TEAP. Toluene was added at an initial concentration of 10 μM.

DAYS

TOLUENE IN HEADSPACE IN PARTS PER MILLION

METHANE IN HEADSPACE IN PARTS PER MILLION

killed with heat, there was little loss of toluene over time. After a brief initial lag, the addition of NTA greatly accelerated the loss of toluene over time in sediments containing live microorganisms. As the toluene was metabolized, more toluene was added and it was rapidly degraded. NTA did not stimulate loss of toluene in heat-killed sediments.

In contrast to the sediments in which Fe(III) reduction was the TEAP, toluene was not metabolized over a 15 day incubation period in sediments in which the TEAP was methane production (data not shown). Furthermore, additions of NTA did not stimulate toluene degradation in the methanogenic sediments (data not shown). In order to determine whether the difference in rates of toluene degradation in the methanogenic and Fe(III)-reducing sediments could be attributed to differences in the availability of Fe(III) as an electron acceptor, methanogenic sediments were mixed with an equal volume of methanogenic sediments which had been oxidized under air in order to convert Fe(II) compounds to Fe(III) oxides. In the presence of Fe(III) oxides, methane production was inhibited (fig. 2), presumably because the TEAP had been switched from methane production to Fe(III) reduction. The addition of Fe(III) also greatly stimulated the loss of toluene.

These results suggest two mechanisms in which the degradation of aromatic hydrocarbons may be stimulated in petroleum contaminated aquifers. When Fe(III) oxides are naturally available, it may be possible to enhance contaminant degradation by adding chelators, such as NTA, which make Fe(III) more available for reduction. In methanogenic zones of aquifers in which Fe(III) is not available for reduction, it may be possible to stimulate in situ metabolism of contaminants by emplacing a barrier of sand heavily coated with Fe(III) oxide. This “iron curtain” could have the
Figure 3. U(VI) concentrations over time in mine drainage water and uranium-contaminated ground water in the presence of hydrogenases and cytochrome c₃, with or without added H₂. The initial concentrations of U(VI) in the mine water and ground water were 36 and 0.5 μM, respectively.

Recent studies in our laboratory have demonstrated that cytochrome c₃ is the U(VI) and Cr(VI) reductase in Desulfovibrio vulgaris (Lovley, 1993b). Whole cells of Desulfovibrio desulfuricans were previously shown to effectively treat uranium in mine drainage water from a U. S. Department of Interior site and contaminated ground water from a U. S. Department of Energy site (Lovley and Phillips, 1992b). In order to determine whether cytochrome c₃ could also reduce U(VI) in these waters, cytochrome c₃ was combined with H₂ and hydrogenase as an electron donating system. Cytochrome c₃ readily reduced U(VI) in both waters (fig. 3). There was no U(VI) reduction when the electron donor, H₂, was omitted.

These results demonstrate that cytochrome c₃ can potentially be used to remove uranium from contaminated environments. For example, cytochrome c₃ is...
readily mass produced and could be employed in fixed-enzyme reactors. Furthermore, the gene for cytochrome $c_3$ from *D. vulgaris* has been cloned and expressed in the closely related *Desulfovibrio desulfuricans* (Voordouw and others, 1990) as well as the genetically distant *Rhodobacter sphaeroides* (Cannae and others, 1991). Thus, the ability for microorganisms to reduce U(VI) and Cr(VI) could potentially be genetically combined with other useful metabolic properties such as denitrification and the ability to degrade organic contaminants. This might confer in a single organism the ability to remove not only the contaminant metals but also other important contaminants, such as organic solvents and nitrate that are typically found in wastes bearing these metals. Future studies will evaluate whether genetically engineering an organism to over-express cytochrome $c_3$ will enhance the capacity for metal reduction.

CONCLUSIONS

It is well known that dissimilatory metal reduction has an important influence on the organic and inorganic geochemistry of a variety of sedimentary environments (Lovley, 1991, Lovley, 1993a, Lovley, 1993b). The studies reported here support the recent suggestion (Lovley, 1993a, Lovley, 1993b) that dissimilatory metal reduction may also have practical application for the remediation of some environments contaminated with organic or metal contaminants.

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Effects of Pb and Terminal-Electron-Accepting Processes on Organic Acid Concentrations in Contaminated Aquifer Sediments

By Paul M. Bradley¹, Francis H. Chapelle¹, and Don A. Vroblesky¹

Abstract

The effects of terminal-electron-accepting processes (TEAPs) and dissolved Pb concentrations on carbon mineralization and organic acid accumulation in petroleum-contaminated sediments were examined under aerobic, nitrate reducing, sulfate reducing, and methanogenic conditions. Pb concentrations in the 14 to 60 µg/L range observed in the field significantly inhibited CO₂ production for all TEAPs as well as CH₄ production under methanogenic conditions. However, accumulation of organic acids was more closely related to the dominant TEAP. Acetic, propionic, i-butyric, and n-butyric acids accumulated in methanogenic treatments, whereas only acetic acid was detected in sulfate reducing treatments. As expected, no organic acids were detected under nitrate reducing or aerobic conditions. This pattern parallels field observations in which high concentrations of organic acids (acetic, propionic, i-butyric, and n-butyric acids) were detected in methanogenic zones, but only low concentrations of acetic acid were detected in sulfate reducing zones.

INTRODUCTION

Recent investigations have shown that short-chain organic acids are important in the chemical and physical diagenesis of contaminated and pristine aquifer systems. The accumulation of organic acids in petroleum hydrocarbon-contaminated aquifers has been widely observed (Cozzarelli and others, 1990; Godsy and others, 1992). In pristine aquifer systems, transport of formic and acetic acids from organic-rich confining bed sediments provides the electron donors for iron reduction, sulfate reduction and methanogenesis in adjacent aquifers (McMahon and Chapelle, 1991; Chapelle and McMahon, 1991; McMahon and others, 1992). Furthermore, the production of organic acids in both pristine and contaminated aquifers appears to be linked to sediment diagenesis and the development of secondary porosity (McMahon and others, 1992; Hiebert and Bennett, 1992).

Given the importance of these compounds as electron donors for microbial respiration in aquifers and their potential role in production of secondary porosity in aquifers, the factors affecting the accumulation of short-chain organic acids in ground water merit further investigation. The shallow aquifer underlying a petroleum tank farm near Charleston, South Carolina is characterized by extensive petroleum contamination and localized high concentrations of short-chain organic acids. At this site, concentrations of acetic, propionic, i-butyric, and n-butyric acids as high as 7,910; 110; 3,140 and 796 µM, respectively, have been reported in ground-water contaminated by petroleum hydrocarbon compounds (P.B. McMahon, U.S. Geological Survey, written commun. 1991).

Water chemistry data collected at the site suggests that the high concentrations of organic acids may be associated with high concentrations of Pb. For example, in January 1992 approximately 40 µg/L of dissolved Pb was detected in water from a well characterized by high organic-acid concentrations.

¹U.S. Geological Survey, Columbia, South Carolina
Because heavy-metal inhibition of organic acid consumption under methanogenic conditions has been reported (Jarrell and others, 1987), this data suggests that Pb at the Hanahan site may contribute to organic-acid accumulation by inhibiting respiration.

The presence or absence of Pb is not the only factor that can affect concentrations of organic acids. Methanogenesis is the dominant electron-accepting process within the zone of organic-acid accumulation at Hanahan, and several studies have reported organic-acid accumulation under methanogenic conditions (Cozarelli and others, 1990, Godsy and others, 1992, Grbic-Galic and Vogel, 1987). Thus the potential exists that accumulation of organic acids is also related to the dominant terminal electron accepting process (TEAP).

Available field data are insufficient to determine the relative importance of Pb concentrations and predominant TEAPs on the observed distribution of organic acids at the Hanahan site. In the studies reported here, an integrated laboratory approach is used to investigate the importance of Pb concentrations and predominant TEAPs on observed concentrations of organic acids at this site. The results indicate that the distribution of TEAPs, rather than concentrations of Pb, is the predominant control on the accumulation of organic acids in ground water at this site.

MATERIALS AND METHODS

Sediment samples. Sediment was collected from a petroleum hydrocarbon-contaminated, surficial aquifer underlying a fuel tank farm near Charleston, South Carolina. A zone of heavily contaminated sediment containing millimolar concentrations of organic acids is located immediately north of tank 3. The shallow aquifer at the site is characterized by medium-grained sands underlain by predominantly clayey material at a depth of 6-11 m. At the time of sample collection, the depth to water table was 5.0 m. Recharge to the water table at the site occurs from infiltration of rainwater and from lateral movement of ground water from areas southeast of the facility. Ground water flows northwestward from tank 3 at rates of 60 to 90 m/yr. During 1990-92, the ground water north of tank 3 contained 0.2 mg/L benzene and up to 2.5 mg/L toluene.

Sediment was collected at the water table from a site where concentrations of organic acids were low (EW-12). Sediment was collected with a flame-sterilized hand auger and stored in sterilized jars. Jars were filled with ground water from an adjacent monitoring well and sealed without headspace in order to preserve anaerobic conditions. Additional water was collected without headspace in sterile BOD bottles for use in microcosm slurries. Sediment and water samples were stored at 4 °C in the dark until microcosm experiments were initiated.

Water samples. Water samples for analysis of short-chain organic acids and inorganic constituents were obtained from 5 cm i.d. diameter PVC monitoring wells by means of a teflon bailer. Samples were placed in precleaned glass bottles, chilled to 4 °C, and transported to the laboratory for subsequent analysis. In the field, ground-water pH and dissolved-oxygen concentrations were determined according to Wood (1976) and hydrogen gas concentrations were measured as described by Chapelle and McMahon (1991).

Microcosm experiments. Production of CO₂ and organic acids was investigated for a combination of four TEAPs and six concentrations of Pb. Approximately 17.5 g of saturated sediment (12.5 g dry sediment) was transferred aseptically to 40 mL sterile serum bottles. Stock solutions of Pb were prepared by diluting PbCl₂ in ground water collected from a monitoring well immediately adjacent to the site of sediment sampling. The Pb stocks were adjusted to pH 6.5 and flushed with He to eliminate oxygen. At the time of sediment collection, the ground water from EW-12 contained about 14 μg/L of dissolved Pb. A 5 mL aliquot of the appropriate Pb stock was added to each microcosm to yield added Pb concentrations ranging from 0 to 1,000 μg/L (pH = 6.5). Aerobic treatments were prepared under room atmosphere. Methanogenic treatments were created by flushing continuously with He during sediment transfer and for 5 min prior to sealing with thick butyl rubber stoppers. Results of a preliminary study indicated that EW-12 sediments that were treated in this manner were dominated by methanogenesis. Nitrate and sulfate reducing conditions were created by adding anoxic NaNO₃ or Na₂SO₄ stock solution to yield final concentrations of 2 mM and then flushing with He gas as described above. Triplicate live and a single biologically inactive (amended with HgCl₂ to concentration of 2 mM and autoclaved for 20 min at 121 °C) treatments were created for each combination of Pb and TEAP.
Analytical procedures. Production of CO₂ in treatment bottles was quantified as the change in concentration (relative to initial values) after a 24-hour incubation period. CH₄ production was quantified in the same manner for methanogenic treatments. Headspace CO₂ and CH₄ concentrations were measured on a gas chromatograph with thermal conductivity detection. Dissolved-gas concentrations were estimated using Henry's Law coefficients (Stumm and Morgan, 1981: p 109). Statistically significant differences between treatment means were determined by one-way ANOVA and Tukey's Studentized Range Test (SAS Institute, 1985). The dominant terminal electron accepting process occurring in the treatment bottles was identified by analysis of headspace H₂ gas on a gas chromatograph equipped with a reduction gas detector according to methods described previously (Chapelle and McMahon, 1991, Lovely and Goodwin, 1988).

The extent to which organic acids accumulated was evaluated for aerobic, nitrate reducing, sulfate reducing, and methanogenic treatments containing 0 and 1,000 μg/L of added Pb. To determine which conditions favored the accumulation of organic acids in the presence of a readily degradable substrate, treatment vials were amended (following completion of the CO₂ and CH₄ production experiment) with glucose to a final concentration of 1.0 mM. To determine if the pattern of organic acid accumulation differed significantly in treatments where petroleum hydrocarbons represented the predominant carbon substrate, additional sulfate reducing and methanogenic treatments were created without glucose amendment. Glucose amended and unamended treatments were incubated for approximately 5 days. Subsequently, organic acids were separated by ion-exclusion chromatography and quantified by conductivity detection. Treatment bottles were mixed thoroughly, and porewater was collected and filtered prior to analysis. Acetic, propionic, i-butyric, and n-butyric acids were resolved on a Dionex ICE-AS1 column with 1 μM HCl at a flow rate of 0.8 mL/min. Minimum detection limits under these conditions were 0.5 μM for all analytes.

RESULTS

Organic acids were not detected in the ground water at EW-12, but ground water from MWGS-34B contained concentrations of acetic, propionic, i-butyric, and n-butyric acids of 9,080; 58; 1,462 and 1,071 μM, respectively (table 1). Both sites were characterized by high concentrations of benzene and toluene in the ground water. The maximum Pb concentration observed at EW-12 was approximately 20 μg/L lower than at MWGS-34B.

Table 1. Select characteristics of ground-water from the site of sediment collection (EW-12) and the site at which maximal concentrations of short-chain organic acids were observed (MWGS-34B)

<table>
<thead>
<tr>
<th>PARAMETER</th>
<th>EW-12</th>
<th>MWGS-34B</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO₃ (μM)</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>SO₄ (μM)</td>
<td>31</td>
<td>6</td>
</tr>
<tr>
<td>CH₄ (μM)</td>
<td>1800</td>
<td>2300</td>
</tr>
<tr>
<td>Pb (μg/L)ᵇ</td>
<td>14-19</td>
<td>39</td>
</tr>
<tr>
<td>pH</td>
<td>5.6</td>
<td>5.2</td>
</tr>
<tr>
<td>H₂ (nM)</td>
<td>1-5ᶜ</td>
<td>12-13</td>
</tr>
<tr>
<td>Benzene (ppb)</td>
<td>72</td>
<td>99</td>
</tr>
<tr>
<td>Toluene (ppb)</td>
<td>3400</td>
<td>1900</td>
</tr>
<tr>
<td>Acetic Acid (μM)</td>
<td>&lt;5</td>
<td>9100</td>
</tr>
<tr>
<td>Propionic Acid (μM)</td>
<td>&lt;5</td>
<td>58</td>
</tr>
<tr>
<td>I-Butyric Acid (μM)</td>
<td>&lt;5</td>
<td>1500</td>
</tr>
<tr>
<td>N-Butyric Acid (μM)</td>
<td>&lt;5</td>
<td>1100</td>
</tr>
</tbody>
</table>

ᵃExcept where noted, data are for samples collected in June of 1992.
ᵇGiven as the range of concentrations measured at each site from January to July of 1992.
ᶜRange of H₂ concentrations detected in ground-water from monitoring wells adjacent to EW-12 at time of sample collection.

For all TEAPs examined in this study, the total CO₂ produced in 24 hours decreased with increasing Pb concentration (fig. 1). In the aerobic and nitrate reducing treatments, Pb concentrations in the range of 35-60 μg/L significantly (pF = 0.0001) inhibited CO₂ production. Under methanogenic conditions, CO₂ (fig. 1) and CH₄ (fig. 2) production was significantly inhibited in Pb treatments greater than 50 μg/L. CO₂ production in the sulfate reducing treatments was not significantly affected by Pb additions in the range of 0 to 250 μg/L. In the low Pb treatments, production of CO₂ varied significantly (pF < 0.0001) with the TEAP in the order aerobic > nitrate reducing > sulfate reducing > methanogenic. However, for treatments containing at least 500 μg/L Pb, CO₂ production was significantly higher in the aerobic bottles (pF < 0.0005) but did not differ significantly between nitrate reducing, sulfate reducing, and methanogenic treatments. The concentrations of H₂ gas measured in the anaerobic TEAP treatments were in the range of concentrations reported for natural sediments under nitrate reducing, sulfate reducing, and methanogenic conditions, respectively (table 2).
Figure 1. CO₂ produced in 24 hours as a function of the concentration of Pb added to aerobic, nitrate reducing, sulfate reducing, and methanogenic treatments. For a given TEAP different superscripts denote significantly different subsets according to Tukey's studentized range test (pF < 0.05). The background Pb concentration in the study sediment was approximately 14 μg/L.

Table 2. Concentrations of H₂ gas (nM) detected in anaerobic microcosms incubated with different Terminal Electron Accepting Processes (TEAPs) and Pb treatments

<table>
<thead>
<tr>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>0</td>
<td>4.0</td>
<td>11.5</td>
<td>6.8±4.1</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>10.1</td>
<td>13.5</td>
<td>11.8±2.4</td>
</tr>
<tr>
<td>SO₄</td>
<td>0</td>
<td>3.0</td>
<td>4.0</td>
<td>3.7±0.7</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>3.0</td>
<td>5.4</td>
<td>3.9±1.3</td>
</tr>
<tr>
<td>NO₃</td>
<td>0</td>
<td>0.6</td>
<td>0.8</td>
<td>0.7±0.1</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>1.1</td>
<td>1.7</td>
<td>1.3±0.3</td>
</tr>
</tbody>
</table>

Table 3. Concentrations of short-chain organic acids in microcosms incubated with different Terminal Electron Accepting Processes (TEAP), Pb, and glucose treatments

<table>
<thead>
<tr>
<th></th>
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<tr>
<td>CH₄</td>
<td>+</td>
<td>0</td>
<td>691±522</td>
<td>46±3</td>
<td>48±34</td>
<td>304±231</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>0</td>
<td>97±50</td>
<td>8±6</td>
<td>--</td>
<td>38±30</td>
</tr>
<tr>
<td></td>
<td>+</td>
<td>1000</td>
<td>2±1</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>SO₄</td>
<td>+</td>
<td>0</td>
<td>1±1</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>0</td>
<td>2±1</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td></td>
<td>+</td>
<td>1000</td>
<td>2±1</td>
<td>11±9</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>NO₃</td>
<td>+</td>
<td>0</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>0</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td></td>
<td>+</td>
<td>1000</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>O₂</td>
<td>+</td>
<td>0</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>0</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
</tr>
</tbody>
</table>

With glucose amendment, organic acids accumulated to detectable levels (0.5 μM) in the sulfate reducing and methanogenic treatments but not under aerobic or nitrate reducing conditions (table 3). Sulfate treatments contained trace amounts of acetic acid (<2 μM) and, in the presence of 1.014 μg/L Pb, low concentrations of propionic acid. Under methanogenic conditions, high concentrations of all four acids were observed, and Pb amendment reduced the accumulation of all acids except propionic. Without glucose amendment, the same pattern was observed. Only acetic acid was detected in the sulfate reducing treatments, but all four acids were detected in the methanogenic treatments. The concentrations of organic acids in the methanogenic treatments were approximately an order of magnitude higher in the glucose-amended treatments than in the unamended microcosms.

Table 3. Concentrations of short-chain organic acids in microcosms incubated with different Terminal Electron Accepting Processes (TEAP), Pb, and glucose treatments

a Measured values are means±SD for triplicates.
b Glucose amended (+) or unamended (-) treatments.
c Not analyzed.
DISCUSSION

Pb concentrations above 14 μg/L (background concentration in collected sediments) inhibited carbon mineralization in these petroleum-contaminated sediments. The effect of Pb was apparently TEAP dependent with the greatest inhibition occurring under oxygen and nitrate reducing conditions. The percentage decreases in CO₂ production in the 1,000 μg/L added Pb treatments (relative to background) were 61, 59, 51 and 45 % for aerobic, nitrate reducing, sulfate reducing, and methanogenic conditions, respectively. This observation is consistent with the findings of previous investigators that sulfate reduction is more sensitive to Pb toxicity than methanogenesis (Capone and others, 1983). The lack of inhibition of CO₂ production by low Pb concentrations observed in the sulfate reducing treatments was probably due to a reduction in the concentration of dissolved Pb by precipitation with sulfide. Thus, the Pb treatments reported for sulfate reducing conditions may be overestimates of the actual dissolved concentrations. Even though Pb concentrations in the range observed at the tank farm inhibited CO₂ production in the methanogenic treatments, CH₄ production remained unaffected. It is not clear whether this response is due to a Pb-induced 1) reduction in fermentative CO₂ production, 2) elimination of low levels of competitive CO₂-producing processes such as SO₄ reduction (Capone and others, 1983), or 3) a shift from organic acid-consuming mechanisms such as acetotrophic methanogenesis (simultaneous CO₂ and CH₄ production) toward hydrogenotrophic methanogenesis (simultaneous CO₂ consumption and CH₄ production).

The 20 μg/L difference in maximum Pb concentrations observed between EW-12 and MWGS-34B in January 1992 initially suggested a role for Pb in the build-up of organic acids at MWGS-34B. However, several lines of evidence suggest that Pb concentrations are not a major contributor to observed organic acid accumulation. As discussed above, CO₂ production was reduced by Pb concentrations in the range observed at the site, but CH₄ production remained unaffected (fig. 2). Moreover, addition of Pb under methanogenic conditions appears to inhibit fermentative organic acid-production (table 2) as well as carbon mineralization (fig. 1). Finally, in the more recent water-quality data, Pb remained approximately 14 μg/L at EW-12 and organic acids were not detected while at MWGS-34B organic acid concentrations remained high but Pb was not detected. The lack of detectable Pb in the recent ground-water samples from MWGS-34B diminishes the importance of Pb at this site. Although Pb may be a significant factor affecting carbon mineralization in the petroleum-contaminated sediments at the tank farm, it is unlikely that Pb is a primary contributor to organic acid-accumulation.

An alternative explanation for the variation in organic acid accumulation at the site involves the range of carbon substrates degraded by different TEAPs. Aerobic microorganisms are able to oxidize a wide number of organic substrates, including the short chain organic acids, to CO₂ (Gottschalk, 1986 p.149). Thus, even considering the presence of anaerobic microsites which pervade saturated sediments, it is unlikely that short-chain organic acids would accumulate under predominantly aerobic conditions. Similarly, denitrification allows complete oxidation of the organic substrate to CO₂ (Gottschalk, 1986 p. 123). Moreover, given the greater solubility of NO₃ relative to O₂, it is even less likely that microsites would form in which fermentation products could accumulate. In contrast, the substrates for sulfate reducers and methanogens are primarily the products of fermentative bacteria. Among the sulfate reducers, two groups are generally distinguished: 1) those species which incompletely oxidize higher fermentation products to acetate and 2) those species which are able to oxidize these organic substrates, including acetate, to CO₂ (Gottschalk, 1986 p. 260; Widdel, 1986; Widdel, 1988; Chapelle, 1993). Thus, accumulation of acetate may occur in an anaerobic environment dominated by group 1 sulfate reducers, but in general accumulation of the short-chain acids to high concentrations would not be expected in an environment dominated by a mixed community of sulfate reducers. Unlike other anaerobic respirers, methanogens are able to metabolize only a limited number of organic substrates. The acknowledged substrates for methanogens include H₂ and CO₂, formate, acetate, methanol, and methylated amines (Gottschalk, 1986 p. 252; Oremland, 1988; Chapelle, 1993). Degradation of other fermentation products by methanogenic systems requires a syntrophic association between methanogens and the bacteria which cleave these substrates to acetate, CO₂, and H₂ (Archer and Harris, 1986; Gottschalk, 1986 p. 265; Widdel, 1986). Thus, accumulation of short-chain organic acids may be expected under methanogenic...
conditions in the absence of acetogenic, hydrogenogenic syntrophs. Moreover, since the substrate affinity for acetate (Archer and Harris, 1986; Widdel, 1986) is much lower for methanogens than sulfate reducers, a higher acetate concentration under methanogenic conditions may occur as well.

Several studies have observed an accumulation of short-chain organic acids in petroleum-contaminated sediments under anaerobic conditions. A laboratory investigation of benzene and toluene biodegradation under methanogenic conditions revealed the production of several aliphatic acids, including acetic and butyric acids (Grbic-Galic and Vogel, 1987). In a shallow aquifer system, mg/L concentrations of acetic acid and unidentified C₃-C₆ volatile organic acids were detected in methanogenic sediments immediately down gradient from the source of creosote- and petroleum-containing waste water (Godsy and others, 1992). High concentrations of organic acids, primarily acetic acid, were detected in the methanogenic zone adjacent to a crude-oil spill (Cozarelli and others, 1990).

The results of the current investigation indicate that the TEAP is the primary factor contributing to the accumulation of short-chain organic acids in petroleum-contaminated sediments. As expected, no short-chain organic acids were detected in either the aerobic or the nitrate reducing microcosms. Organic acids accumulated in sulfate reducing and methanogenic microcosms under glucose amended and unamended conditions. Glucose amendment increased the concentration but not the species of accumulated organic acids. A similar response to glucose amendment was reported for methanogenic acid-bog sediments (Goodwin and Zeikus, 1987). All four acids accumulated under methanogenic conditions, but only trace amounts of acetic acid were detected in the sulfate-reducing treatments.

The relation between organic acids accumulation and TEAP observed in the lab study is consistent with what is observed in the field. In this study, H₂ gas concentrations were used as a primary indicator of the TEAP which dominated the sediment microbial processes, because H₂ is a short lived (rapidly turned-over) and ubiquitous intermediate of microbial metabolism. Thus, the H₂ concentration measured at a site is characteristic of the dominant metabolism at that location (Lovely and Goodwin, 1988) while, in contrast, respiratory products such as sulfide and CH₄ can be transported over great distances by ground water flow. The 12-13 nM H₂ gas concentrations observed at MWGS-34B, the site of organic acid accumulation, are in the range characteristic of methanogenic sediments (Chapelle and McMahon, 1991, Lovely and Goodwin, 1988). Moreover, the low SO₄ (6 μM) concentration measured at MWGS-34B is consistent with methanogenesis. The H₂ concentrations at EW-12 (1-5 nM) were indicative of predominantly sulfate reducing conditions and organic acids were not detected at this site. The higher SO₄ concentration at EW-12, also, was consistent with sulfate reducing conditions. These observations, which are consistent with previous studies (Grbic-Galic and Vogel, 1987; Cozzarelli and others, 1990; Godsy and others, 1992), suggest that the accumulation of high concentrations of organic acids, especially the butyrates, primarily result from the biodegradation of petroleum hydrocarbons in predominantly methanogenic environments.

REFERENCES


Shifting of Terminal-Electron-Accepting Processes in a Petroleum-Hydrocarbon-Contaminated Aquifer

By Don A. Vroblesky and Francis H. Chapelle

Abstract

Measurements of dissolved hydrogen and other biologically active solutes in ground water from a shallow petroleum hydrocarbon-contaminated aquifer indicate that the distribution of microbial terminal electron accepting processes (TEAP's), such as methanogenesis, sulfate reduction, and ferric-iron reduction, is highly dynamic in both time and space. Delivery of sulfate to previously methanogenic zones by infiltrating recharge or lateral transport can result in a TEAP shift from methanogenesis to sulfate reduction. Conversely, lack of recharge and consumption of available sulfate can result in a shift from sulfate reduction to methanogenesis. Temporal shifts between sulfate and ferric-iron reduction were also observed.

INTRODUCTION

Identifying the dominant terminal-electron-accepting processes (TEAP's) in contaminated ground water is an important step in determining the fate of contaminants. Although petroleum hydrocarbons are most readily degraded under aerobic conditions, it is apparent that degradation also occurs under methanogenic (Grbic-Galic and Vogel, 1987), sulfate (SO$_4$)-reducing (Beller and others, 1992; Edwards and others, 1992; Edwards and Grbic-Galic, 1992), ferric iron (Fe$^{3+}$)-reducing (Lovley and others, 1989), and nitrate (NO$_3$)-reducing (Hutchins and others, 1991) conditions. Furthermore, there is evidence that biodegradation rates depend on TEAP's. For example, Smolenski and Suflita (1987) showed that the rate of biodegradation of several cresol isomers was faster under sulfate-reducing conditions than under methanogenic conditions. This observation raises the possibility that differences in anaerobic TEAP conditions may directly affect microbial degradation rates of hydrocarbon contamination in ground water.

Baedecker and others (1993) observed areal differences in TEAP conditions in oil-contaminated ground water, and they noted that changes in concentrations of microbially active constituents in the oil-contaminated ground water implied that the TEAP was changing from iron reduction to methanogenesis over a 5-year period. Little work has been done, however, in examining short-term variations of TEAP's in contaminated ground water or in determining the implications of these changes on biodegradation of the contamination. The purpose of this paper is to examine spatial and temporal variations in TEAP's in a shallow, petroleum-hydrocarbon-contaminated aquifer.

Background

Historically, methods used to identify TEAP's in ground-water systems have focused on documenting the consumption of particular terminal-electron acceptors, such as nitrate (Baedecker and Back, 1979) or sulfate (Thorstenson and others, 1979), that support microbial metabolism. Alternatively, metabolic end products, such as methane (CH$_4$) (Thorstenson and others, 1979; Baedecker and others, 1988), sulfide (H$_2$S) (Rightmire and Hanshaw, 1973; Jackson and Patterson, 1982), or ferrous iron (Fe$^{2+}$) (Baedecker and others, 1988), have been used as a criteria to identify the dominant TEAP's. Because some electron acceptors, such as SO$_4$, can be replenished from mineral sources, and because most final products

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1U.S. Geological Survey, Columbia, South Carolina
(methane, Fe$^{3+}$, and sulfide) are transported by flowing ground water, these methods are commonly equivocal.

The use of hydrogen ($H_2$) -- a transient intermediate product of anaerobic microbial metabolism -- as an indicator of predominant TEAP's was introduced by Lovley and Goodwin (1988). This approach has been used to document the zonation of TEAP's in various systems by Chapelle and Lovley (1990), Chapelle and McMahon (1991), and Chapelle and Lovley (1992). These studies indicate that $H_2$ concentration ranges of 5 to 25 nmol/L are characteristic of methanogenesis, 1 to 4 nmol/L are characteristic of $SO_4$ reduction, and 0.1 to 0.8 nmol/L are characteristic of Fe$^{3+}$ reduction. Because $H_2$ is an extremely transitory intermediate, with a half life of less than a minute (Conrad and others, 1987), it is an ideal constituent for documenting temporal as well as spatial variations in TEAP's. In this study, $H_2$ concentrations were used in conjunction with concentrations of other microbially active solutes to document the spatial and temporal variations in TEAP's.

**Description of Study Area**

The study area consisted of a petroleum-tank farm, referred to hereafter as the facility, in Hanahan, South Carolina, and the area surrounding the facility (fig. 1). The site is underlain by unconsolidated Pleistocene sediments composed of quartz sand and lenses of clay. The base of the Pleistocene sediments is at a depth of about 11 m. Below the Pleistocene sediment is a dense clay, approximately 65 m thick, that vertically isolates the shallow ground-water-flow system. A thin layer (about 5 cm) of carbonate material covers the bermed basins containing the fuel tanks.

The Pleistocene sediment functions as an unconfined water-bearing zone, but clay lenses locally produce confined-flow conditions. This surficial...
aquifer is recharged by rainwater infiltration. Periods of intense rainfall can increase ground-water levels by 0.6 m over several days. Ground-water levels declined about 1.2 m during a drought between late September 1991 to early January 1992.

Ground-water discharge at the site is by evapotranspiration and by flow to nearby drains and streams. The predominant direction of ground-water flow beneath the facility is northwestward (fig. 1). Ground water at the site is contaminated with benzene, toluene, ethyl benzene, and xylene (collectively termed BTEX) (fig. 1).

Although Fe\(^{3+}\)-rich grain coatings are common in uncontaminated parts of the aquifer, the sediment in petroleum-contaminated parts of the aquifer is white to light gray with no Fe\(^{3+}\)-rich grain coatings. The substantial precipitation of Fe\(^{3+}\) in surface water where contaminated ground water discharges attests to widespread removal of Fe\(^{3+}\) from the aquifer sediments by reduction in the contaminant plume.

**Methods**

Temporal variations in TEAP's were monitored in the surficial aquifer at wells for varying lengths of time during June 1991 - January 1993. The two wells discussed here are screened at the water table (well MW-40A) and from about 4.9 to 7.9 m below the water table (well MW-5A). Data used to discuss temporal variation in spatial zonation of TEAP's were collected from 19 wells in late June to early July 1991 and from 27 wells in November 1992.

Water samples for analysis of BTEX were collected by slowly filling 40-mL glass vials from a bottom-discharge bailer. The vials were allowed to overflow several seconds and were then preserved with hydrochloric acid and capped with Teflon-lined septa. If aeration of a sample was suspected, or if bubbles were observed in a vial, the sample was replaced. On the day of collection, the water samples for BTEX were delivered to a private laboratory for analysis.

Immediately following collection of BTEX samples from each well, samples for inorganic ions were collected by peristaltic pump. Well water was pumped through a 0.45-μm filter into sample-rinsed polyethylene bottles. Ferrous iron was analyzed using a field colorimetric method. NO\(_3\) and SO\(_4\) were separated in the laboratory by anion-exchange chromatography and quantified by conductivity detection. CH\(_4\) samples were collected using a syringe with an attached 0.45-μm filter to inject 5 mL of water into septed vials. CH\(_4\) samples were refrigerated to minimize microbial activity. CH\(_4\) was quantified by flame ionization detection gas chromatography. Dissolved CH\(_4\) concentrations were calculated using Henry's Law coefficients (Stumm and Morgan, 1981).

Ground-water H\(_2\) samples were collected using the bubble-strip method of Chapelle and McMahon (1991). A stream of water was pumped from the well through a gas-sampling bulb at a rate of about 600 mL per minute. An injected bubble of nitrogen in the bulb asymptotically collected H\(_2\) and other soluble gases until equilibrium was achieved. Once equilibrium was achieved (less than 5 percent change in 5 minutes, which occurred within 15 minutes), gas was extracted from the bulb by syringe. H\(_2\) was measured on a gas chromatograph equipped with a reduction gas detector. The detection limit of this method was approximately 0.01 μL/L. H\(_2\) samples were not collected if the ground water at the well was found to be aerobic.

**RESULTS**

Ground water collected from wells MW-5A and MW-40A contained differing concentrations of several constituents (table 1). Temporal variations in the concentrations of H\(_2\) were found in the ground water at each of the wells (figs. 2 and 3).

In addition, temporal variations in the spatial zonation of H\(_2\) concentrations were found. Temporal

**Table 1. Range of concentrations of relevant microbially affected constituents in ground water at wells MW-5A and MW-40A for June 1991-January 1993**

<table>
<thead>
<tr>
<th>Well</th>
<th>Hydrogen (nmol/L)</th>
<th>Methane (μmol/L)</th>
<th>Sulfate (mg/L)</th>
<th>Ferric iron (mg/L)</th>
<th>Nitrate (mg/L)</th>
<th>BTEX (μg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MW-5A</td>
<td>1.2-12.5 (8)</td>
<td>1,120-1,770 (5)</td>
<td>0.01-2.6 (8)</td>
<td>6.0-30.0 (7)</td>
<td>&lt;0.01-0.12 (8)</td>
<td>9.40 (7)</td>
</tr>
<tr>
<td>MW-40A</td>
<td>0.6-1.4 (4)</td>
<td>80-680 (5)</td>
<td>12.1-23.17 (5)</td>
<td>2.8-8.4 (6)</td>
<td>0.14-0.99 (5)</td>
<td>40-770 (7)</td>
</tr>
</tbody>
</table>
changes in ground-water H₂ concentrations differed over short distances horizontally (<5 m) and vertically (<3.5 m) at this site. Moreover, distinct changes were found in the areal distribution of H₂ concentrations from June-July 1991 to November 1992 (fig. 4).

DISCUSSION

The ground-water-chemistry data from wells screened in different areas of ground-water contamination show that the predominant TEAP's change with time. The changes differed from site to site, depending on differences in the ground-water chemistry in various parts of the contamination. Well MW-5A is an example of a site where concentrations of BTEX are low (9-40 µg/L), concentrations of dissolved Fe²⁺ are high (up to 40 mg/L) and concentrations of SO₄ are low (up to 2.6 mg/L). In January 1992, the H₂ concentration (1.7 nmol/L) (fig. 2A) indicated that SO₄ reduction was the predominant TEAP. Supporting evidence for SO₄ reduction was the presence of dissolved SO₄ (0.88 mg/L) and the decreasing concentrations of SO₄ (fig. 5B) in ground water at well MW-5A over the next few months. In July and November 1992, the H₂ concentration increased (9.2 and 15.4 nmol/L, respectively), indicating that the predominant TEAP in the ground water at well MW-5A had changed to methanogenesis (fig. 2A). The SO₄ concentrations (0.14 and 0.2 nmol/L, respectively) were apparently too low to support SO₄ reduction as the predominant TEAP. By January 1993, the SO₄ concentration had increased to 2.6 mg/L (fig. 2B). The corresponding decrease in H₂ concentration (to 1.2 nmol/L) indicated that the presence of SO₄ had resulted in a shift in the predominant TEAP from methanogenesis back to SO₄ reduction (fig. 2A).

Well MW-40A is an example of an area where ground water became oxygenated after a period of heavy rainfall. When the well was first sampled in July 1992, the H₂ concentration (1.4 Nm/L) was in the range characteristic of SO₄ reduction (fig. 3A). In August 1992, however, a period of rainfall provided substantial recharge to the aquifer. By the time well MW-40A was sampled in early September 1992, the ground water at the site had become oxygenated. The corresponding sharp decrease in dissolved Fe²⁺
Figure 4. Areal distribution of terminal-electron-accepting processes, based on interpretation of H₂ measurements in ground water for (A) June-July 1991 and (B) November 1992.
concentrations (8.4 mg/L in July 1992 to 2.8 mg/L in September 1992) (fig. 3B) indicates that Fe^{2+} was oxidized to Fe^{3+} and precipitated out of solution as grain coatings. By late September 1992, the dissolved oxygen had been depleted. At least part of the electron flow from oxidation of organic matter was sequestered by Fe^{3+} reduction, as implied by the decrease in H\textsubscript{2} concentration to 0.7 nmol/L, in the range of H\textsubscript{2} concentration characteristic of Fe^{3+} reduction (fig. 3A). A corresponding increase in dissolved Fe^{2+} may not have occurred because of precipitation of iron sulfide or other minerals.

**SUMMARY AND CONCLUSIONS**

The predominant TEAP in anaerobic ground water contaminated with petroleum hydrocarbons at a tank farm in Hanahan, South Carolina, varies with time as electron acceptors are depleted or added. During times when little or no SO\textsubscript{4} or oxygen are introduced to the ground water by recharge from rainfall, the available oxygen, Fe\textsuperscript{3+}, and SO\textsubscript{4} can be depleted by respiring bacteria, leaving methanogenesis as the predominant TEAP. Introduction of oxygen, from rainfall infiltration, into the anaerobic parts of the aquifer can cause precipitation of Fe\textsuperscript{3+} as grain coatings. Once the oxygen is depleted, Fe\textsuperscript{3+}-reducing bacteria can take advantage of the precipitated Fe\textsuperscript{3+} to sequester the electron flow from degradation of organic compounds. If the water table is lowered below the zone of Fe\textsuperscript{3+} availability, electron flow can be sequestered by less efficient TEAP's, such as SO\textsubscript{4} reduction. Introduction of SO\textsubscript{4} into a methanogenic part of the aquifer can cause a shift in the predominant TEAP to SO\textsubscript{4} reduction.

**REFERENCES**


Preliminary Assessment of Jet Fuel Contamination of an Atoll Aquifer

By Gordon W. Tribble¹, Roger W. Lee², Duane S. Wydoski³, Jill D. Torikai¹, and Charles D. Hunt, Jr.¹

Abstract

Jet fuel spilled in 1991 on the atoll island of Diego Garcia (Chagos Archipelago, Indian Ocean) has contaminated one of the fresh ground-water lenses on the island. Freshwater lenses on the island are unconfined and strongly influenced by tidal oscillations in sea level. The U.S. Geological Survey is using a multidisciplinary approach to (1) evaluate contaminant migration and, (2) determine the geochemical processes that affect contaminant degradation. A network of water-level recorders is being used to determine the effect of a hydraulic control scheme on the water-table configuration and contaminant transport. The water table near the spill is 1 to 2 feet above mean sea level and undergoes diurnal oscillations of as much as 4 feet in response to ocean tides.

Geochemical characterization of the aquifer will help to resolve ambient and fuel-affected levels and types of microbial oxidation. This information is useful to determine the need for, and type of, remediation of residual contamination after efforts to remove the fuel by pumping are completed. Initial data from the first of three planned trips indicate that natural levels of microbial oxidation are sufficient to deplete O₂ in all aquifer waters. Concentrations of CO₂, CH₄, and H₂S indicate that the natural levels of microbial oxidation are enhanced by the presence of hydrocarbon contaminants. An evaluation of the rates, mechanisms, and limits of microbial oxidation in the aquifer will require additional sampling and physical measurements to assess hydraulic processes such as aquifer properties and the response of ground-water flow to different recharge and withdrawal conditions.

INTRODUCTION

Diego Garcia is a low, 20 ft maximum altitude, coral atoll of the Chagos Archipelago in the central Indian Ocean at latitude 7°S and longitude 72°E (fig. 1). It is a part of the British Indian Ocean Territory and the site of a U.S. Navy Support Facility (Navy) jointly administered by the United Kingdom and the United States. The facility is used to support military operations in the Indian Ocean and nearby regions. The atoll has about 3,000 inhabitants. In 1991, fuel leaking from a buried pipeline introduced contaminants into a water-table aquifer underlying the Air Operations area (fig. 1, U.S. Navy, oral commun., 1991). At the Navy's request, the U.S. Geological Survey (USGS) is evaluating the hydrologic and geochemical aspects of the fuel spill to provide a conceptual basis for aquifer remediation. The USGS acknowledges and thanks the U.S. Navy for funding and logistic support. This paper describes the contaminated site, lists tasks currently underway, and presents some preliminary findings with an emphasis on the geochemical aspects of the project.

About 98 percent of all drinking water on the atoll is supplied by thin freshwater lenses in the Cantonment and Air Operations areas of Diego Garcia. The water table is typically 5 ft below land surface and the aquifer material is unconsolidated calcareous sediments. The two freshwater lenses are less than about 60 ft thick and less than 1.5 mi² in area.
Figure 1. Location of study area and types of wells on Diego Garcia.
Ground-water withdrawal from the lenses averages about 1.2 Mgal/d. About 30 percent of pumpage is from the Air Operations area, near the site of the spill (fig. 1). Although average annual rainfall is 106 in., the quantity of freshwater stored in ground water is small and the aquifer is highly susceptible to saltwater intrusion owing to seasonal and interannual variations in rainfall (Hunt, 1991). To avoid saltwater upconing, more than 100 shallow horizontal production wells have been constructed to skim freshwater from the two lenses and distribute the effect of pumpage over a broad area. Salinity acceptable for drinking has been maintained over the past decade, with chloride concentrations ranging between 30 and 130 mg/L. Before May 1991, pumpage from the Air Operations area was 0.4 Mgal/d (C.D. Hunt, USGS, written commun., 1993).

Aquifers on atolls respond dynamically to both physical and chemical processes. Variable quantities of recharge, combined with relatively low storage, cause the freshwater part of the aquifer to shrink and expand in response to seasonal and interannual variations in rainfall (Hunt, 1991). Sea-level fluctuations owing to tides are transmitted through the aquifer and cause diurnal oscillations of several feet in the water table. The oscillations also create a broad transition zone between infiltrated rainwater and underlying saltwater (Buddemeier and Holladay, 1977; Hunt and Peterson, 1980; Wheatcraft and Buddemeier, 1981; Ayers and Vacher, 1986; Anthony and others, 1989). The oxidation of organic matter is pervasive in many atoll aquifers, resulting in naturally low concentrations of dissolved oxygen, elevated concentrations of dissolved inorganic carbon, and production of hydrogen sulfide (Buddemeier and Oberdorfer, 1986). Changes in water chemistry associated with the oxidation of organic matter change the saturation state of the water with respect to the carbonate minerals that constitute the aquifer. Organic matter oxidation and carbonate mineral diagenesis cause water chemistry to differ from that expected from simple conservative mixing of rainwater and seawater.

Several characteristics make this site attractive for a multidisciplinary study of contaminant hydrogeochemistry: (1) The seawater surrounding the atoll provides sharp physical and geochemical delineation to the aquifer; (2) constantly warm subsurface temperatures provide a stable environment favorable to microbial metabolism; (3) aquifer waters are derived solely from seawater and rainwater, so the stoichiometry and extent of specific reactions can be deduced from the nonconservative characteristics of selected constituents; (4) the calcium carbonate mineralogy of the aquifer provides a geochemically simple, albeit reactive, matrix; and (5) contamination at the site is thought to have originated from a single leak, so complications associated with multiple releases over time and space are not likely. Logistics, however, are difficult because of the distance between Diego Garcia and the United States.

**PROBLEM**

In the mid-1980s, an aircraft-refueling support base was constructed at the Air Operations area (fig. 1). In May 1991, a leak of JP-5 jet fuel from a pipeline beneath the apron was detected. Because of the history of use, the leak probably occurred sometime after January 1991. Much of the spill is overlain by several feet of compacted carbonate sand and gravel fill covered with 18 in. of reinforced concrete.

The volume of spilled fuel is unknown. Following discovery of the spill, the Navy started a program of exploratory drilling and fuel recovery. As of January 1993, more than 120,000 gal of fuel has been recovered by pumping free-floating fuel from shallow pits. Several nearby horizontal water-supply wells in the Air Operations area have been shut down so that pumping will not entrain fuel towards the wells. The wells remain shut down pending the results of ongoing studies. The lost production capacity is about 0.5 Mgal/d, about 40 percent of the present island-wide pumpage of ground water. To offset the loss, withdrawal of ground water has been increased elsewhere, although this could raise the salinity to levels unacceptable for drinking if the increased pumpage coincides with a drought. Consequently, the Navy intends to restore lost pumping capacity through a program of aquifer remediation.

This project has focused on the physical processes that determine the transport of contaminants and the geochemical processes that affect contaminant degradation. A combination of ground-water modeling, hydrologic monitoring, and chemical sampling is being used to determine these processes and to evaluate the effectiveness of remedial actions. The USGS is providing the Navy information on methods of aquifer protection and the hydrologic aspects of free-product recovery. Hydrologic
monitoring during free-product recovery is planned for use in evaluating the effectiveness of anticipated water-table adjustments and for providing large-scale information on hydraulic properties of the atoll aquifer. After the end of free-product recovery, a substantial mass of free fuel is expected to remain in the aquifer at residual saturation. In anticipation of the need for remediation following free-product recovery, the USGS is also evaluating geochemical considerations relevant to hydrocarbon degradation within the aquifer.

HYDRAULIC DIVERSION AND MONITORING

Sparse water-level data indicate that the water table is relatively flat but has a small gradient from the spill area towards the west (PRC Toups, 1983; C.D. Hunt, USGS, written commun., 1991). Withdrawal of freshwater from the water-supply wells could lower the water table enough to substantially change the direction of ground-water flow. In an attempt to inhibit movement of fuel from the spill towards the water-supply wells, freshwater has been injected since April 1992 into several water-supply wells close to the spill. This injection is being done to create a mound in the water table and modify the hydraulic gradient in the aquifer, thus changing the direction of ground-water flow near the spill to divert contaminants to the north and away from the water-supply wells. A line of six free-product recovery wells is planned for the northern edge of the refueling apron; each recovery well will have a pump to lower the water table and a fuel skimmer (U.S. Navy, oral commun., 1992).

In October 1992, 10 water-level observation wells were installed (fig. 1). Each well has been equipped with a data logger that records water levels at 10 minute intervals. The water-level data are downloaded weekly by Navy personnel. The high frequency of data collection has been selected to measure the tidal dynamics of the aquifer. An example of the observed water-level fluctuations is shown in figure 2. Well WL-2 is 20 ft deep and about 300 yards from the lagoon; the depth to water is about 5 ft below land surface. The water-level data show an average head of 1.75 ft above mean sea level. The ratio of the amplitudes between water-level fluctuations in well WL-2 and ocean tides was 0.72, and the time lag between peak high or low tide in the ocean and well WL-2 was 20 minutes.

GEOCHEMICAL CHARACTERIZATION

Nests of monitoring wells were installed at five sites in October 1992 to characterize geochemical processes within the aquifer, evaluate hydrocarbon degradation, and monitor site restoration (fig. 1). At each site, 4 or 5 wells have depths that range from 15 to 55 ft below ground surface. The wells are constructed of 2-in. inside-diameter (i.d.) PVC and have a screened interval of 5 ft. At each site, a vapor probe is used to sample soil gas from 3 to 3.5 ft below land surface. At unpaved sites where rainfall can infiltrate, soil-water probes have been installed at depths of 2 and 3 ft below land surface to sample fluids from the unsaturated zone. Following discovery of the spill, several exploratory wells were constructed of screened 2 in. (i.d.) PVC to a depth of about 5 ft below the water table. These exploratory wells are used to detect free and dissolved fuel at the top of the water table.

In February 1993, the monitoring wells were sampled using a submersible pump with a casing packer. pH, O₂ concentration, and temperature of water samples were measured in a closed cell at the site. H₂S concentration was determined by titration following field preservation. Samples for determination of major ions and nutrients were filtered in a field laboratory and analyzed at the University of Hawaii. Aqueous and vapor-phase measurements of CO₂, O₂, N₂, CH₄ and volatile aromatic carbon compounds were made using portable gas chromatographs equipped with thermal-conductivity.
and photoionization detectors. The exploratory wells were sampled using disposable bailers. Much of the data from the initial trip are not yet available and all results are considered as preliminary pending additional sampling and analysis. However, several trends are evident from the preliminary data.

The approximate areal extent of free-phase and dissolved-phase fuel in proximity to the spill is shown in figure 3. As of February 1993, fuel was detected several hundred feet from the spill and found as a dissolved phase as deep as 40 ft below the water table. Of particular concern is that free-phase and dissolved-phase fuel have migrated about half the distance from the spill to several water-supply wells. Additional data are needed to evaluate the effectiveness of the hydraulic control system in retarding or diverting the migration of contaminants towards the water-supply wells.

There is evidence that microbial oxidation is greater where the aquifer is contaminated by the fuel. Microbial respiration will initially consume O₂ and switch to other metabolic pathways such as sulfate reduction (producing H₂S) and methanogenesis (producing CH₄) after O₂ is depleted (Chapelle, 1993). Cross sections of benzene, CH₄, CO₂, and H₂S concentrations in the saturated zone at monitoring sites S-1, S-3, and S-5 are shown in figure 4. Sites S-1 and S-3 are contaminated with jet fuel, whereas site S-5 is uncontaminated. Concentrations of O₂ are typically less that 0.3 ppm in the ground-water samples from the study area. Ground-water samples with the highest O₂ concentrations (0.6-0.3 ppm) were
Figure 3. Location of sites with and without (A) free-phase fuel and (B) dissolved fuel, in February 1993.
Figure 4. Chemical sections from well sites S-1 to S-5. Benzene concentrations in parts per billion, H$_2$S concentrations in parts per million, CH$_4$ and CO$_2$ in atmospheres of partial pressure.
from the contaminated site S-1. Additional sampling is needed to determine if this is a result of sampling error or incomplete oxic respiration in that part of the aquifer. Concentrations of CH$_4$, CO$_2$, and H$_2$S are low in both surface seawater and rainwater; the high concentrations of CH$_4$, CO$_2$, and H$_2$S in water from all well waters demonstrates that substantial microbial respiration is occurring within the aquifer. The contaminated sites S-1 and S-3 tended to have much greater concentrations of CH$_4$, CO$_2$, and H$_2$S than do the uncontaminated site S-5. It thus seems that natural levels of microbial oxidation are sufficient to deplete O$_2$ in aquifer waters, and the oxidation of fuel is proceeding through other metabolic pathways such as methanogenesis and sulfate reduction.

Future work needs to focus on determining the extent and metabolic pathways of microbial processes in both the saturated and unsaturated parts of the aquifer. Of particular interest are the microbial oxidation of fuel, the factors limiting microbial respiration, and the relation between microbial oxidation and carbonate-mineral diagenesis. Complete analysis of data from the February 1993 trip, as well as future data as it becomes available should permit a thorough characterization of both natural and fuel-enhanced geochemical processes in the aquifer.

**SUMMARY**

The USGS has begun a project to investigate a subsurface spill of JP-5 jet fuel that has contaminated one of the freshwater lenses at Diego Garcia. Part of this project is to provide hydrologic data to evaluate the migration of both free-phase and dissolved-phase fuel constituents towards water-supply wells and to facilitate the recovery of free fuel. The hydrologic data are obtained from a network of 10 water-level observation wells. Preliminary analysis of data reveals oscillations in the water table of as much as 4 ft associated with the rise and fall of ocean tides. The tidal signal is propagated rapidly through the aquifer with a relatively high efficiency, indicating that the aquifer is moderately to highly permeable.

Another part of this project entails the characterization of geochemical processes within the aquifer to evaluate methods of remediating residual contamination after the free fuel has been removed. Of particular interest is the determination of microbial processes within the aquifer and the effect of the fuel on such processes. Preliminary data indicate that natural microbial oxidation of organic matter is occurring throughout the aquifer and results in the depletion of O$_2$, and the production of CO$_2$, H$_2$S, and CH$_4$. Areas contaminated by fuel have higher concentrations of the products of microbial respiration (CO$_2$, H$_2$S, CH$_4$) than uncontaminated areas, indicating that the fuel is being oxidized by microbial activity.

**REFERENCES**


Microbial Degradation of Nitrotoluenes in Surface Soils and Aquifer Sediments, Weldon Spring, Missouri

By Francis H. Chapelle and Paul M. Bradley

Abstract

Surface soils and underlying aquifer material from a nitrotoluene-contaminated site at Weldon Spring, Missouri, were evaluated for the potential of indigenous microorganisms to transform 2,4,6-trinitrotoluene (2,4,6-TNT), 2,4-dinitrotoluene (2,4-DNT) and 2,6-dinitrotoluene (2,6-DNT). The results indicate that the microbial communities are capable of rapidly metabolizing 2,4-DNT, 2,6-DNT and 2,4,6-TNT. In most cases, complete disappearance of the source compound was achieved within 20 to 70 days. These results indicate that in-situ bioremediation may be a viable alternative for treating contaminated soils and ground water. Furthermore, the results suggest that the presently observed nitroaromatics contamination of ground water is unlikely to be a relic of past (50 years before present) waste-disposal practices, but rather reflects continual leaching of nitroaromatics from contaminated soils.

INTRODUCTION

The manufacture, loading, assembling, and packing of munitions have resulted in nitrotoluene contamination of soils and ground water at many sites throughout the United States. The process of separating the desired 2,4,6-trinitrotoluene (2,4,6-TNT) product from the numerous impurities created during the manufacturing process generates large quantities of "red-water" wastes that contained 2,4-

1U.S. Geological Survey, Columbia, South Carolina
dinitrotoluene (2,4-DNT)-and 2,6-dinitrotoluene (2,6-DNT) as well as other nitrotoluene isomers. During World War II, red water was commonly disposed of by direct discharge to streams at the Weldon Spring munitions manufacturing facility in Missouri. These past waste-disposal practices resulted in widespread nitroaromatics contamination of soils and ground water at the Weldon Spring site.

The presently observed nitroaromatics contamination of ground water at the Weldon Spring site (Schumacher and others, 1992) may be a relic of past waste-disposal practices. However, this hypothesis suggests that nitroaromatics are stable in the aquifer system and not subject to significant microbial degradation. On the other hand, if the aquifer system contains microorganisms capable of degrading nitroaromatics, a continuous source of nitroaromatics (such as leaching from cocontaminated surface soils) is indicated. In either case, one key to resolving the source of the presently observed nitroaromatic contamination of ground water is to evaluate the potential of indigenous microorganisms to degrade nitroaromatics.

Numerous recent investigations have focused on microbial degradation of nitrotoluenes (Carpenter and others, 1978; Kaplan and Kaplan, 1982; Hallas and Alexander, 1983; Liu and others, 1984; Fernando and others, 1990; Spanggord and others, 1991; Higson, 1992; Spiker, 1992; Valli and others, 1992; Funk and others, in press). However, these investigations utilized artificial sources of microbial communities such as sewage and activated sludge systems (Carpenter and others, 1978, Hallas and Alexander 1983, Liu and others, 1984), land farming and composting (Kaplan and Kaplan 1982, Spiker and others, 1992, Funk and others, in press), as well as isolated cultures of bacteria (McCormick and others, 1976, Spanggord and others,
or fungi (Fernando and others, 1990, Valli and others, 1992). Surprisingly, however, little is known about the capability of native microorganisms to transform nitrotoluenes *in-situ*. In this report, we examine the potential for *in-situ* biodegradation of nitrotoluenes by surface soils and aquifer sediments at a contaminated site in Weldon Spring, Missouri. We also examined the effect of nitrotoluene additions on sediment CO₂ production to evaluate the impact of nitrotoluene contamination on overall microbial community metabolism at the site.

**MATERIALS AND METHODS**

The ability to transform 2,4-dinitrotoluene, 2,6-dinitrotoluene and 2,4,6-trinitrotoluene was examined using a contaminated surface soil (red tank), an uncontaminated surface soil (top soil), fractured carbonate bedrock material (carbonate), and material from a weathered, semi-consolidated water-bearing zone (residuum) that occurs at the top of the carbonate aquifer. The highly contaminated red-tank soil was collected within an inactive red-water holding-lagoon in which TNT concentrations range from 1,000 to 10,000 mg/kg soil. The top soil was collected at an adjacent site with no detectable nitrotoluene contamination and no history of nitrotoluene exposure. The residuum and carbonate aquifer materials were collected from areas contaminated by red water in the past, and where leaching of nitroaromatics from contaminated soils may be presently occurring. Concentrations of 2,6-DNT and 2,4-DNT in the aquifer are presently in the parts per billion range.

Sediment samples were incubated statically in 35 mL serum vials containing 20 g wet soil or sediment and 20 mL of nitrotoluene solution. The final dissolved concentrations of the nitrotoluenes were 100-150 μM. The treatments were created with an air headspace and sealed with Teflon coated butyl rubber stoppers. Triplicate experimental samples, a single live control (not sterilized and without nitrotoluene addition) and a single dead control (with nitrotoluene addition and sterilized by amendment with 5 mM HgCl₂ and autoclaving for 60 min) were prepared for each combination of sediment and nitrotoluene treatment. The vials were incubated in the dark at room temperature and periodically sampled for dissolved nitrotoluenes and headspace CO₂ for approximately 70 days.

Nitrotoluene analyses were made as follows: Approximately 12 hours before sample collection and analysis, the treatment vials were shaken by hand to thoroughly mix the interstitial and standing water. To sample, about 0.5 mL of standing water was removed, filtered (0.2 μm pore size) and analyzed by high pressure liquid chromatography. The sample volume was replaced with 99.9 percent O₂ gas. Nitrotoluene analyses was performed on a Beckman Ultrasphere ODS C₁₈ column at 40 °C with a acetonitrile:distilled water:methanol mobile phase. The 2,4-DNT and 2,6-DNT analyses were made isocratically with a 15:45:40 acetonitrile:distilled water:methanol mobile phase. TNT was determined by gradient elution with a 15:80:5 acetonitrile: distilled water:methanol mobile phase ramping up to 47:48:5 over 25 minutes and holding for 5 minutes (method by Chris Lindley, U.S. Geological Survey). All compounds were detected by UV absorption at 250 nm. Peak areas were quantified by calibration against known standards (Aldrich Chemical Co.).

Headspace CO₂ concentrations were determined as an indicator of microbial community metabolism. A 0.5 mL headspace sample was removed and analyzed by thermal conductivity detection gas chromatography. The sample volume was replaced with 99.9 percent O₂. Peak areas were quantified by calibration against known standards (Scotty II, Scott Gas Co.).

**RESULTS**

The pattern of microbial-community metabolism (CO₂ production) varied between soil and sediment samples, but, with the exception of the top soil (2,4-DNT) treatment, community CO₂ production did not differ between the TNT, 2,4-DNT, or 2,6-DNT treatments for a given soil or aquifer sediment. In the residuum, for example (fig. 1), CO₂ production was similar for each compound. Significantly, however, the carbonate and residuum samples produced CO₂ only in the nitrotoluene-amended treatments. Without nitrotoluene addition, the CO₂ production did not differ from that in the sterile controls (fig. 1). In the red-tank soils, CO₂ production was greatest in the live controls (fig. 1). In the red-tank soils, CO₂ production was greatest in the live controls (without nitrotoluene amendment). Addition of 2,4-DNT, 2,6-DNT or 2,4,6-TNT inhibited CO₂ production in this soil. In contrast, addition of 2,4-DNT or 2,4,6-TNT to the top soil did not inhibit CO₂ production relative to that of the live control. However, addition of 2,4-DNT did appear to reduce the top soil microbial metabolism.
During the 70-day incubation period, all three nitrotoluenes were degraded by the surface soils and aquifer sediments (figs. 2-4). The concentrations of nitrotoluenes remaining in each treatment are expressed as a percent of the initial dissolved concentration (100-150 μM). The carbonate microbial community degraded 2,4,6-TNT more rapidly than the dinitrotoluenes, but the concentrations of all nitrotoluenes were reduced by at least 80 percent during incubation. There was no observable lag in the degradation of nitrotoluenes by the carbonate sediments. Although the concentrations of 2,4-DNT and 2,4,6-TNT in the residuum microcosms were reduced below the detection limit (0.1 μM), about 45 percent of the added 2,6-DNT remained at day 70 (fig. 2). The lag preceding a detectable decrease in nitrotoluene concentrations in the residuum treatments varied from 8 days (2,4-DNT) to about 22 days (2,4,6-TNT). About 95 percent of the 2,4-DNT and 2,4,6-TNT in the red tank microcosms was removed without a lag by day 30 (fig. 3). After a 20 day lag, the concentration of 2,6-DNT decreased to the detection limit by the end of the experiment. In contrast, approximately 95 percent of the 2,6-DNT and 2,4,6-TNT in the top soil microcosms was removed (without lag) within 22 days, while complete degradation of 2,4-DNT was delayed by about 30 days (fig. 4).

**DISCUSSION**

The results indicate that microbial communities associated with surface soils and underlying aquifer material at Weldon Springs, Missouri are capable of rapidly metabolizing 2,4-DNT, 2,6-DNT and 2,4,6-TNT. In most cases, complete disappearance of the source compound was achieved within 20 to 70 days. In this study, degradation of the source nitrotoluene was followed by accumulation of the associated aminonitrotoluenes (data not shown). However, subsequent decreases in the dissolved concentrations of these intermediates indicates that the aminocompounds are biodegradable as well. These results indicate that in-situ bioremediation may be a viable alternative for cleanup of nitrotoluene-contaminated aquifers and soils.

From an environmental impact point of view, degradation of a contaminant is desirable only if the products are innocuous or at least less problematic than the source compound. Ideally, the contaminant is completely degraded to CO₂ (or CH₄ and CO₂ under anaerobic conditions) during bioremediation. At present, only the white-rot fungus, *Phanaerochaete chrysosporium*, has been reported to degrade nitrotoluenes to CO₂. Approximately 35 percent of
The $^{14}$C from labeled 2,4,6-TNT and 2,4-DNT was recovered as $^{14}$CO$_2$ during incubation with *P. chrysosporium* (Fernando and others, 1990, Valli and others, 1992). However, this organism has been shown to be sensitive to high concentrations of 2,4,6-TNT (Spiker and others, 1992). The majority of studies have reported accumulation of aminonitrotoluens (McCormick and others, 1976, Hallas and others, 1983, Liu and others, 1984, Funk and others, *in press*) or highly toxic and biologically inert azoxy polymers (Kaplan and Kaplan 1982, Funk and others, *in press*). Two lines of indirect evidence suggest that the Weldon Springs microbial communities may be capable of more complete degradation. The fact that aminonitrotoluens initially accumulated and subsequently diminished with time (data not shown) indicates that these compounds are transitory intermediates of nitrotoluene degradation by the Weldon Springs microbial communities. Moreover, the fact that CO$_2$ production by carbonate and residuum sediments was significant only in the presence of nitrotoluenes (fig. 1) is highly suggestive of complete degradation to CO$_2$. However, because these sediments contain carbonate material, the
The primary motivation for undertaking these studies was to determine (1) if the residuum and carbonate aquifer lack microorganisms capable of degrading nitroaromatics, in which case the presently observed nitroaromatic contamination of ground water could be a relict of past contamination, or (2) if the residuum and carbonate aquifers contain microbial populations capable of nitroaromatics degradation, in which case the observed ground-water contamination may indicate a continuous nitroaromatics source from the contaminated soils. Available evidence supports the second hypothesis and suggests that nitroaromatics are being continually leached into the aquifer from contaminated soils. These results also suggest that naturally occurring biodegradation will tend to limit the transport of nitroaromatic contaminants by ground at this site.

REFERENCES


Depletion of Nitrogen-Bearing Explosives Wastes in a Shallow Ground-water Plume near Hawthorne, Nevada

By A.S. Van Denburgh¹, D.F. Goerlitz², and E.M. Godsy²

Abstract

Liquid explosives wastes from the emptying and washout of military projectile and bomb casings were discharged into unlined disposal pits north of Hawthorne, Nevada. The explosives involved at this arid study area were ammonium picrate, during 1952-58, and trinitrotoluene (TNT) plus ammonium nitrate, during 1964-68. Percolation from the pits entered unconsolidated, heterogeneous sedimentary deposits in which clay- to gravel-size particles predominate. The water table at and downgradient from the pits was from 1-1/2 to 6-1/2 meters below land surface during the study. The shallow ground water moves northwestward at an average linear velocity of about 130 meters per year.

A shallow plume of ground water containing 3 to 130 milligrams per liter of dissolved-nitrogen species, as nitrogen, extended more than 1,700 meters northwest of the northernmost pits. Either ammonium or nitrate dominated at sample sites within 300 meters of the pits; farther downgradient in the plume, nitrate was the most abundant. Overall, the plume contained about 3 megagrams of dissolved nitrogen downgradient from the pits. The proportions of sodium and bicarbonate ions increased downgradient, relative to chloride and sulfate ions. Saturated sedimentary deposits within the plume generally had greater concentrations of organic nitrogen, ammonium, and organic carbon than did the adjacent sediments.

The maximum linear velocities for the dissolved explosives-waste components (a measure of their mobility) ranged from more than 77 meters per year for nitrate to less than 20 meters per year for picrate, with velocities of TNT and ammonium in between. The downgradient movement of nitrate may not have been impeded by microbiological or geochemical processes. For the other dissolved components, in contrast, the following depletion mechanisms are proposed: TNT, microbial transformation to inorganic nitrogen and carbon species, and probable sorption of organic transformation products; ammonium, sorption, and probable oxidation by nitrifying bacteria; and picrate, microbial alteration to picramic acid, then mineralization to inorganic nitrogen and carbon species. The reactions that depleted TNT, ammonium, and picrate in the ground water may also have enriched the proportions of sodium and bicarbonate ions in the plume. Overall, the Hawthorne study shows that natural microbiological and geochemical processes can degrade or retard the transport of large quantities of toxic, chemically complex, nitrogen-rich explosives wastes over distances of hundreds of meters, leaving nitrate as the only residual nitrogen-bearing component of the ground-water plume.

INTRODUCTION

The military ammunition plant near Hawthorne, Nev., was commissioned in 1930 to fill, store, and empty explosives containers such as projectile and bomb casings. A variety of liquid wastes from the emptying and washout (demilitarization) processes were discharged into unlined disposal pits at several sites within the 700-km² plant during the last six decades. Ground water beneath the disposal sites moves generally northwestward toward Walker Lake, a 140-km² closed-basin body of saline water that is used for recreation (fig. 1). Because much of the lake is outside the plant boundary, the U.S. Department of the Army asked the U.S. Geological Survey (USGS)
in 1978 to evaluate the extent and magnitude of contamination in shallow ground water between the then-northernmost demilitarization site and the lake (the nearest demilitarization facility upgradient from that site was almost 4,000 m to the southeast). Explosives processed at the site included ammonium picrate, trinitrotoluene (TNT), and ammonium nitrate.

This paper describes principal results of that study and of an earlier one by the USGS immediately downgradient from disposal pits at the same site. Discussed herein are the hydrogeologic setting of the overall 2-km² study area, chemical character of the shallow ground water and host sedimentary deposits within and adjacent to the contaminant plume, differing mobilities of the several dissolved explosives-waste components, and mechanisms by which those components were altered and depleted as the shallow ground water moved toward Walker Lake. These discussions are based on data collected from about 40 shallow exploratory wells (depths, 7-14 m) drilled adjacent to and downgradient from the northernmost pits during 1975-78. Most of the water-chemistry analyses were made on samples collected from the wells in 1977 or 1979. At the time of study, results were documented in unpublished administrative reports; more recently, selected aspects of the investigations were described briefly by Van Denburgh and Goerlitz (1987) and by Goerlitz (1992, p. 325-330). The more extensive discussion herein was inspired by the possible transfer value of the Hawthorne results at a time of increasing USGS involvement in studies of waste-disposal contamination at military facilities. Details regarding procedures used at Hawthorne to drill the exploratory wells and to collect and analyze the sediment cores and water samples therefrom are available in files of the USGS (333 W. Nye Lane, Carson City, NV 89706).

We are particularly grateful to Don Cavin, Louie Dellamonica, Bill Glenzer, Don Gruwell, Floyd Justus, Dell Mortensen, and Joe Viani of Hawthorne (all but Mr. Viani are current or retired employees of the ammunition plant), who provided a blend of historical perspective, material assistance, and genuine hospitality that made our task so much easier.
GEOGRAPHY, HYDROLOGY, AND WASTE DISPOSAL

The study area (fig. 2) is on the gently northwestward-sloping floor of Walker Lake Valley about 1,220 m above sea level. Adjacent mountains to the west and east are 1,000 to 2,000 m higher. Precipitation on the valley floor averages only about 100 mm/yr; atop the highest adjacent range, the average may not be much greater than 300 mm/yr [on the basis of an estimated long-term average at the briefly operated Mount Grant storage gage, 2,700-m altitude (Van Denburgh and Glancy, 1970, p. 10)]. Consequently, all streams in this arid to semiarid area are ephemeral downgradient from the mountain fronts.

Sedimentary deposits beneath the study area are unconsolidated to partly consolidated aggregations of lacustrine and alluvial clay, silt, sand, and gravel; their cumulative thickness is 800 to 1,000 m (D.H. Schaefer, U.S. Geological Survey, written commun., 1985). Shallow exploratory wells drilled during the study penetrate generally heterogeneous deposits in which clay- to gravel-size particles predominate. A distinctive impermeable clay unit underlies these deposits; the top of the clay ranges from 7-1/2 to at least 11 m below land surface.

The water table, which areally varied from 1-1/2 to 6-1/2 m below land surface during the period of study, slopes generally northwestward (gradient, about 5.5 m/1,000 m; see fig. 2). The average horizontal hydraulic conductivity of saturated deposits overlying the clay unit is on the order of 7 m/d, as estimated from results of slug tests. The slug-test data were analyzed by R.L. Carman (U.S. Geological Survey, written commun., 1979) using the procedure described by Cooper and others (1967). The average effective porosity of the deposits within the plume may be 10 to 12 percent based on moisture-content measurements of sediment samples from below the water table. These values indicate that the shallow ground water moves downgradient at an average linear rate of 120 to 140 m/yr, on the basis of the equation given by Lohman and others (1972, p. 14).

The then-northernmost demilitarization site at the ammunition plant was used beginning in about 1952, and large but unrecorded volumes of liquid waste were generated (historical information herein is based mostly on written and oral communications from William K. Glenzer and Dell L. Mortensen during 1976-79). Explosives at the site were ammonium picrate (formal name, ammonium 2,4,6-trinitrophene nolate) from projectile casings emptied during about 1952-58 and TNT (2,4,6-trinitrotoluene) plus ammonium nitrate from bomb casings emptied during 1964-68. The solubility of these toxic compounds in water ranges widely, from 130 mg/L at 20°C for TNT (Gordon and Hartley, 1992, p. 327) to 11,000 mg/L and 1,920,000 mg/L at 20°C for ammonium picrate and ammonium nitrate, respectively (Sax and Lewis, 1987, p. 165 and 163).

CHEMICAL CHARACTER OF SHALLOW GROUND WATER AND SATURATED SEDIMENTARY DEPOSITS

Although sodium and sulfate were the dominant ions in all ground water sampled at the study area, three chemical traits—the areal distributions of dissolved-nitrogen species (fig. 2), dissolved-solids concentrations, and major ions—delineate the extent of a plume of contaminated ground water downgradient from the demilitarization site. The contrasting concentrations listed in table 1 provide a “chemical signature” for water in the plume, relative to the adjacent, presumably uncontaminated ground water.

Downgradient from the northernmost pits, the relative amount of sodium (Na+) in the plume increased in comparison to the more conservative chloride (Cl-) and sulfate (SO4^2-) ions: at mid-plume wells C and D (fig. 2), the proportion of Na+ relative to Cl- and SO4^2- was about 40 percent greater than it was at upgradient well B; at well E, it was 80 percent greater than at well B. The proportion of bicarbonate (HCO3-) in the plume also increased downgradient, relative to Cl- and SO4^2-: at well E, it was more than 100 percent greater than at upgradient wells C and D.

Concentrations of dissolved explosives-waste components also changed downgradient from the pits. TNT decreased from about 500 µg/L at well A to less than the detection limit (2 µg/L) at well D. Picrate concentrations were less than the 2-µg/L detection limit at and downgradient from well C (unfortunately, picrate analyses were not made at earlier-sampled wells closer to the disposal pits). Down-plume changes in the concentrations of dissolved-nitrogen species and TNT are shown in figure 3. At the center of the plume, less than about 300 m from the six northernmost pits, ammonium-nitrogen concentrations exceeded those of nitrate-nitrogen; elsewhere in the plume, nitrate consistently dominated.
Figure 2. Water-table contours and concentrations of dissolved nitrogen and trinitrotoluene (TNT) in exploratory wells downgradient from waste-disposal pits.
At well C, the total concentration of dissolved-nitrogen species decreased with increasing depth below the water table (fig. 3); measured TNT concentrations at the site decreased similarly. Downward dispersion of the explosives wastes is limited by the impermeable clay that underlies most or all of the plume 10 to 11 m below land surface.

Calculated rates of dissolved-nitrogen transport as of the late 1970's, in Mg/yr, were about 0.7 for a transverse section across the plume at well B (fig. 2), about 0.4 at a section through well C, and about 0.1 at a section through well D. The dissolved-nitrogen content of the entire ground-water plume downgradient from the northernmost pits is estimated to have been on the order of 3 Mg.

Saturated sedimentary deposits within the plume generally had somewhat greater to much greater concentrations of nitrogen species and organic carbon than did adjacent sediments, as indicated in table 2. All analyses for TNT and picrate yielded concentrations below the 25 µg/kg detection limit, but such analyses are not available for deposits upgradient from well C, in the area where concentrations of dissolved-nitrogen species—including TNT—were highest (figs. 2 and 3). Comparison of the available nitrogen data for sediments and companion ground water within the plume indicates that almost all of the organic nitrogen and ammonium were components of the sedimentary deposits, whereas the nitrate was a component of the interstitial fluids.

**Plume of contaminated ground water**

- Water-table contour—Shows altitude of water table, April 1979. Contour interval, 2 meters. Datum is sea level
- Direction of ground-water flow
- Line of equal dissolved-nitrogen concentration—Approximately located. Interval, in milligrams per liter, is variable

**Exploratory well where water contained 2 micrograms per liter of TNT or more**—Number is dissolved-nitrogen concentration, in milligrams per liter. Symbol (<, less than) indicates approximate value from earlier study terminated before final sample was collected from well. Letter identifies key well. Range of concentrations at well C in part B is for three screened intervals of differing depth (see hydrogeologic section in fig. 3)

**Exploratory well where water contained less than 2 micrograms per liter of TNT**—Number is dissolved-nitrogen concentration, in milligrams per liter. Symbol (<) as defined above. Letter identifies key well

**Unsampled exploratory well**—Depth-to-water data used to delineate water-table contours

**Feature of demilitarization facility**—1, empty-and-washout building; 2, large disposal pits, about 900 meters upgradient from well C (ammonium-picrate wastes during 1952-58, TNT and ammonium-nitrate wastes during 1964-68); 3, concrete and metal troughs; 4, six northernmost pits, about 450 meters upgradient from well C (ammonium picrate during 1957-58, TNT and ammonium nitrate during 1964-68); 5, three additional pits (used little, if any)

**DEPLETION OF DISSOLVED EXPLOSIVES WASTES**

The mobilities of individual explosives-waste components differed considerably, as indicated in table 3. Nitrate, the most mobile, had a linear velocity more than three times that of picrate, the least mobile. For any dissolved component of the contaminant plume, a linear velocity appreciably slower than the linear rate of ground-water flow indicates that the migration of that component is being retarded (attenuated) by depletion mechanisms. Thus, table 3 indicates that dissolved TNT, ammonium, and especially picrate, were depleted downgradient from the disposal pits.

**Trinitrotoluene**

Microbial transformations probably were the key mechanisms for removal of TNT from the ground-water plume. Investigations at well A (fig. 2) revealed that aerobic bacteria capable of altering TNT to aminotoluene compounds (Won and others, 1974, p. 515-516; McCormick and others, 1976, p. 956) were present. In addition, a large, strictly anaerobic microbe population (10^9 to 10^10 organisms per 100 mL), including sulfate-reducing bacteria, was found at well A, and 4-amino-2,6-dinitrotoluene was detected along with TNT at well C. The amine-substituted intermediate products are known to be co-metabolized under anaerobic conditions (Roberts and others, 1993; Cheng and others, 1993),
Table 1. Chemical character of ground water within and adjacent to the contaminant plume
[Concentrations in milligrams per liter, except as noted; µg/L, micrograms per liter; <, less than]

<table>
<thead>
<tr>
<th>Constituent or property</th>
<th>Contaminant plume</th>
<th>Adjacent ground water</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Maximum</td>
<td>Minimum</td>
</tr>
<tr>
<td>Dissolved solids</td>
<td>2,800</td>
<td>2,200</td>
</tr>
<tr>
<td>Selected major ions:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium</td>
<td>950</td>
<td>580</td>
</tr>
<tr>
<td>Sulfate</td>
<td>1,400</td>
<td>1,100</td>
</tr>
<tr>
<td>Chloride</td>
<td>180</td>
<td>130</td>
</tr>
<tr>
<td>Nitrogen (N) species:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Recoverable organic N</td>
<td>17</td>
<td>0.3</td>
</tr>
<tr>
<td>Nitrate as N</td>
<td>44</td>
<td>2.7</td>
</tr>
<tr>
<td>Nitrite as N</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>Ammonium as N</td>
<td>75</td>
<td>0.0</td>
</tr>
<tr>
<td>Total recoverable N</td>
<td>130</td>
<td>3.1</td>
</tr>
<tr>
<td>Carbon:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Organic</td>
<td>4.9</td>
<td>1.9</td>
</tr>
<tr>
<td>Inorganic</td>
<td>160</td>
<td>60</td>
</tr>
<tr>
<td>Explosives (µg/L):</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trinitrotoluene</td>
<td>500</td>
<td>&lt;2</td>
</tr>
<tr>
<td>Picrate</td>
<td>&lt;2</td>
<td>&lt;2</td>
</tr>
</tbody>
</table>

1Carbon content of bicarbonate and carbonate.

presumably to ammonium, carbon dioxide, and other products, depending on which potential microbial electron acceptors—such as sulfate, or bicarbonate, or ferric iron—are available.

Sedimentary deposits cored at wells C and D contained no detectable TNT but had, on average, 2-1/2 times as much organic nitrogen as cored deposits adjacent to the plume—about 180 mg/kg compared to 70 mg/kg. The sorbed organic nitrogen may have consisted of amino-substituted intermediate products, such as 4-amino-2,6-dinitrotoluene and 2,4-diamino-6-nitrotoluene, or dimerized or polymerized azoxy compounds (Roberts and others, 1993, p. 142).

Picrate

Microbial alteration probably was responsible for the depletion of dissolved picrate near the disposal pits. Microorganisms can effectively alter picrate to picramic acid (Won, 1977). This alteration product is, in turn, vulnerable to metabolism by the resident microbial population, yielding dissolved inorganic nitrogen species and carbon dioxide. These decomposition products may have contributed to the elevated nitrate concentration and bicarbonate enrichment, respectively, in ground water at downgradient well E.

Ammonium

Sorption, and probably microbial oxidation (nitrification), depleted ammonium in the ground-water plume. Sediment cores from well C contained an average ammonium-nitrogen concentration as much as 14 times that of cored deposits adjacent to, and farther downgradient within, the plume (about 33 mg/kg compared to 2.4 mg/kg). Thus, sediments at and upgradient from well C appear to have sorbed ammonium from the ammonium picrate and ammonium nitrate wastes. Clay-mineral sorption of ammonium in exchange for sodium would at least partly explain the sodium enrichment detected in the plume downgradient from well B.
Figure 3. Concentrations of dissolved nitrogen species at exploratory wells A-E within the contaminant plume. At well C, range of concentrations in graphs is for three screened intervals of differing depth.
Table 2. Chemical and physical character of saturated sedimentary deposits within and adjacent to the contaminant plume\(^1\) [mg/kg, milligrams per kilogram, dry weight; \(\mu g/kg\), micrograms per kilogram, dry weight; <, less than]

<table>
<thead>
<tr>
<th>Constituent or property</th>
<th>Contaminant plume</th>
<th>Adjacent deposits</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Maximum</td>
<td>Minimum</td>
</tr>
<tr>
<td>Clay + silt (percent by weight)</td>
<td>29</td>
<td>4</td>
</tr>
<tr>
<td>Water (percent by weight)</td>
<td>16</td>
<td>8</td>
</tr>
<tr>
<td>Nitrogen (N) species (mg/kg)(^2):</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Recoverable organic N</td>
<td>440</td>
<td>11</td>
</tr>
<tr>
<td>Nitrate plus nitrite as N</td>
<td>6.4</td>
<td>.2</td>
</tr>
<tr>
<td>Ammonium as N</td>
<td>80</td>
<td>1.3</td>
</tr>
<tr>
<td>Total recoverable N</td>
<td>440</td>
<td>73</td>
</tr>
<tr>
<td>Carbon (mg/kg):</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Recoverable organic</td>
<td>800</td>
<td>100</td>
</tr>
<tr>
<td>Inorganic</td>
<td>3,800</td>
<td>&lt;50</td>
</tr>
<tr>
<td>Explosives ((\mu g/kg)):</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trinitrotoluene</td>
<td>&lt;25</td>
<td>&lt;25</td>
</tr>
<tr>
<td>Picrate</td>
<td>&lt;25</td>
<td>&lt;25</td>
</tr>
</tbody>
</table>

\(^1\)Data are for cores collected below water table at, adjacent to, and downgradient from well C (fig. 2; data are not available for deposits between well C and disposal pits). Chemical analyses indicate combined concentrations for particulate components and interstitial ground water.

\(^2\)Maximum or minimum concentrations for each nitrogen species were not necessarily measured in same sample.

At well E, principal nitrogen-bearing contaminants are thought to have been related to ammonium picrate wastes, yet nitrate is the dominant dissolved-nitrogen species (fig. 3). The nitrate may have resulted from oxidation of ammonium by nitrifying bacteria (the dissolved-oxygen content of ground water was not measured during the study) as well as from decomposition of picramic acid following microbial alteration of picrate.

**IMPLICATIONS OF DOCUMENTED DEPLETION**

Most dissolved components of explosives-demilitarization wastes that percolated to the shallow ground-water system at the arid study area were at least partly depleted within a relatively short distance (on the order of hundreds of meters) downgradient from the disposal pits. This was particularly true for the nitrogen-bearing organic constituents (TNT, picrate, and their organic degradation products).

The overall effectiveness of depletion is suggested by the downgradient decrease in the total amount of dissolved nitrogen: vertical, transverse segments of the entire plume one longitudinal meter thick at wells B, C, and D (figs. 2 and 3) would have contained 5, 3, and 1 kg of dissolved nitrogen, respectively. (Other factors that undoubtedly contributed to this 80-percent decrease were longitudinal dispersion and fluctuations in contaminant input with time.)

Regardless of the depletion mechanisms involved, the Hawthorne study shows that natural microbiological and geochemical processes can degrade or retard the transport of large quantities of toxic, chemically complex, nitrogen-rich explosives wastes, leaving nitrate as the only residual nitrogen-bearing component in the ground-water plume.
**Table 3. Summary of contrasting mobilities and depletion mechanisms for dissolved explosives-waste components of ground-water plume**

[>, greater than; <, less than]

<table>
<thead>
<tr>
<th>Component</th>
<th>Travel time as of 1979&lt;sup&gt;1&lt;/sup&gt; (years)</th>
<th>Distance traveled as of 1979&lt;sup&gt;2&lt;/sup&gt; (meters)</th>
<th>Linear velocity&lt;sup&gt;3&lt;/sup&gt; (meters per year)</th>
<th>Proposed depletion mechanism(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrate&lt;sup&gt;4&lt;/sup&gt;</td>
<td>22</td>
<td>&gt;1,700</td>
<td>&gt;77</td>
<td>Presumably little if any depletion.</td>
</tr>
<tr>
<td>Trinitrotoluene</td>
<td>15</td>
<td>&gt;450 &lt;1,100</td>
<td>&gt;30 &lt;73</td>
<td>Microbial transformation to inorganic products; probable sorption of organic transformation products.</td>
</tr>
<tr>
<td>Ammonium</td>
<td>22</td>
<td>&gt;450 &lt;1,100</td>
<td>&gt;20 &lt;50</td>
<td>Sorption; probable nitrification.</td>
</tr>
<tr>
<td>Picrate</td>
<td>22</td>
<td>&lt;450</td>
<td>&lt;20</td>
<td>Microbial alteration to picramic acid, then metabolic degradation to inorganic products.</td>
</tr>
</tbody>
</table>

<sup>1</sup>Based on reported first year of disposal at six northernmost disposal pits (ammonium picrate, 1957; TNT and ammonium nitrate, 1964). (See figure 2 and text.)

<sup>2</sup>Linear distance between northernmost pits and wells C (about 450 meters), D (about 1,100 meters), and E (about 1,700 meters). (See figure 2.)

<sup>3</sup>Linear velocity of ion or molecule at leading edge of “cloud” for each constituent within plume. (“Linear velocity” refers to net migration distance along straight line, as opposed to circuitous flow path travelled by interstitial water molecules and solutes.) In comparison, estimated average linear rate of ground-water flow is thought to be 120 to 140 meters per year. Velocities listed here for explosives-waste components are slightly refined from those given by Van Denburgh and Goerlitz (1987).

<sup>4</sup>Nitrate at well E is assumed to have originated from microbial degradation of ammonium picrate wastes; if, instead, it is from ammonium nitrate, linear velocity would exceed 110 meters per year.

**REFERENCES**


Reaction of Arsenic Minerals and Gold Ores with Alkaline Cyanide Solutions

By Walter H. Ficklin\textsuperscript{1}, Geoffrey S. Plumlee\textsuperscript{1}, and John B. McHugh\textsuperscript{1}

Abstract

Gold ores often contain significant quantities of arsenic (As). The As may occur in several different mineral forms and/or oxidation states. The most common As minerals are arsenopyrite (FeAsS), orpiment (As\textsubscript{2}S\textsubscript{3}), and realgar (AsS) but some deposits may contain oxidized forms of arsenic (arsenates) and more exotic minerals, such as enargite (Cu\textsubscript{3}AsS\textsubscript{4}). During heap leaching with alkaline cyanide solutions, some As is dissolved from these minerals. At pH values equivalent to those found in heap-leach solutions, the presence of cyanide increases the concentration of arsenic that dissolves by a factor of 4 to 100 for various forms of As. Formation of thiocyanate is one factor that enhances the dissolution of arsenic from sulfide minerals. Orpiment reacts more strongly with cyanide solutions than realgar and much more strongly than arsenopyrite.

INTRODUCTION

Many gold ores contain significant quantities of arsenic (As). The As may be present in several different mineral forms and oxidation states. The most common As minerals are arsenopyrite (FeAsS), orpiment (As\textsubscript{2}S\textsubscript{3}), and realgar (AsS) but some deposits may contain oxidized forms of arsenic (arsenates) and more exotic minerals, such as enargite (Cu\textsubscript{3}AsS\textsubscript{4}). During heap leaching with alkaline cyanide solutions, As is extracted from ores, sometimes in significant quantities. Concentrations of As in various heap-leach solutions collected from operations in Colorado and Nevada are presented in table 1. Some of these concentrations exceed U.S. Environmental Protection Agency and state drinking water regulations.

The agent responsible for dissolution of As by alkaline cyanide solutions is not known with certainty. The pH of heap-leach solutions ranges from 10 to 12, and the minerals may dissolve because of the action of alkali and (or) the cyanide in solution.

As is an important element to be considered in heap leaching for gold recovery because its dissolution becomes a disposal problem when the heap is no longer used for gold recovery. Furthermore, the dissolution of As minerals may account for excessive cyanide consumption during the heap-leaching process. If leaks develop in heap-leach pads, the As could become an environmental contaminant in soil, alluvium, and ground water.

In this paper we describe the effect of cyanide and alkaline solutions on the dissolution of orpiment, realgar, arsenopyrite and some poorly characterized forms of As-bearing tailings, which may be remined to recover gold that was not recovered in the first processing of the ore.

Table 1. Typical arsenic concentrations determined in heap-leach solutions from selected operations in Nevada and Colorado [Concentrations are in milligrams per liter; number following State denotes different samples from each State]

<table>
<thead>
<tr>
<th>Site</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nevada 1</td>
<td>30</td>
</tr>
<tr>
<td>Nevada 2</td>
<td>.5</td>
</tr>
<tr>
<td>Colorado 1</td>
<td>.3</td>
</tr>
<tr>
<td>Colorado 2</td>
<td>&lt;.01</td>
</tr>
<tr>
<td>Colorado 3</td>
<td>.07</td>
</tr>
</tbody>
</table>
MATERIALS AND METHODS

Orpiment and realgar samples were obtained from the Getchell Mine in Nevada. Arsenopyrite was supplied by Steven Sutley of the U.S. Geological Survey (USGS). Oxidized and unoxidized samples of tailings from Whitewood Creek, South Dakota, were obtained from Kim Goddard of the USGS. The gold reference standard sample was obtained from David Grimes of the USGS.

Reagent-grade sodium hydroxide and sodium cyanide were used to prepare the necessary solution for this study. Analysis of As in samples was performed by graphite furnace atomic-absorption spectrophotometry (Ficklin, 1983). Analysis of thiocyanate (SCN−) in samples was performed by the method presented in Standard Methods for the Examination of Water and Wastewater (American Public Health Association, 1985, p. 348).

Analysis of As species (As(III) and As(V)) in samples was performed by the method of Ficklin, (1983). Iron concentration was determined by flame atomic-absorption spectrophotometry (Aruscavage and Crock, 1987).

EXPERIMENTAL

Experiment 1

Experiment 1 was carried out to determine whether the extraction of arsenic is enhanced by cyanide solution. In order to do this, 0.5 g each of oxidized (3,000 ppm As) and unoxidized (4,000 ppm As) Whitewood Creek tailings and the gold reference material, which was a sample of gold ore from the Pinson Mine, Nev. (DGPM1 containing 180 ppm As), were extracted by four solutions. The solutions used were 20 mL of sodium hydroxide solution of pH 10.85, 20 mL of 500 ppm cyanide solution (pH-10.85), 20 mL of 0.1N sodium hydroxide, and 20 mL of 0.1 N sodium hydroxide that contained 500 ppm cyanide. The samples were placed in capped glass centrifuge tubes, and allowed to react for 1 week with occasional shaking. A duplicate set was reacted for 2 weeks. The resulting extracts were examined for total As concentration.

Experiment 2

Samples of pulverized orpiment (0.1 g) were placed in eight centrifuge tubes. Forty mL of 500 ppm cyanide solution was added to each tube. One of the samples was allowed to react for 30 minutes with occasional shaking. Another was allowed to react for 24 hours with occasional shaking. The remaining six samples were opened, each in succession at approximately 48-hour intervals until about 500 hours had passed. Each solution was measured for total As, As(III), As(V), and SCN−. Similar experiments were conducted with realgar (0.1 g) and arsenopyrite (0.2 g). Iron concentration in the solutions generated by the reaction of arsenopyrite also was measured.

RESULTS AND DISCUSSION

The dissolution of As from gold-bearing materials in alkaline cyanide solutions may be due to the extractive nature of alkaline solutions or to reaction of the substrate with cyanide. In order to determine which of these processes occurs, arsenic-bearing samples were treated, as described in experiment 1. Results of these experiments are presented in figure 1.

In solutions generated by experiment 1 having a pH of 10.85, but without cyanide, only a small amount of As was extracted. In the cyanide solution of the same pH, approximately 100 times the amount of As was extracted from the oxidized tailings and unoxidized tailings. The amount of As extracted from the gold ore sample (DGPM1) was approximately four times greater with cyanide solution (fig. 1A). Data for samples extracted with alkali solutions having a pH of 13 are presented in figure 1B. At this pH, the amount of As that was extracted is not enhanced by the presence of cyanide solutions. Strong alkaline solutions will extract As regardless of the concentration of cyanide; but, with the pH values that are likely to prevail in heap-leach pads, cyanide has a significant effect on the extraction of As.

The significant increase in the dissolution of As from the unoxidized tailings at a pH of 10.85 suggests that the dissolution of sulfide-bearing As minerals by cyanide may be due to the reaction of cyanide with the sulfide part and not the As part of the mineral.

The percentage of As extracted from each mineral type, described above in experiment 2, is presented in figure 2. In similar alkaline cyanide solutions, orpiment is much more soluble than realgar, which, in turn, is much more soluble than arsenopyrite. The analytical results for the concentrations of As species, total As, SCN−, and Fe (arsenopyrite only) for timed extractions of orpiment, realgar, and arsenopyrite are presented in figures 3A,B,C. The extraction of As with 500 ppm
Figure 1. Extraction of arsenic from three different arsenic-bearing materials for 1 and 2 weeks at (A) pH of 10.85 and (B) pH of 13. WWCOX is oxidized tailings from Whitewood Creek S.D., WWCRED is unoxidized tailings from Whitewood Creek, S.D., and DGPM1 is a sample from the Pinson Mine, Nev.

cyanide solution produced As(III), As(V), and an unidentified As compound from orpiment and realgar, but only As(V) from arsenopyrite. The concentration of the unidentified As compound can be calculated as the difference of the total As minus the sum of As(III) and As(V). $\text{As}_2\text{S}_3$ reacts with alkaline solutions according to the following reaction (Hogness and Johnson, 1957):

$$\text{As}_2\text{S}_3 + 4\text{OH}^- = \text{AsS}_3^{3-} + \text{AsO}_2^- + \text{H}_2\text{O}; \quad (1)$$

in water $\text{As}_2\text{S}_3$ reacts according to the following equation:

$$2\text{HAsO}_2 + 3\text{H}_2\text{S} = \text{As}_2\text{S}_3 + 4\text{H}_2\text{O}. \quad (2)$$

The solubility product constant for reaction 2 is $2.1 \times 10^{-22}$. Based on equation 1, the unidentified As compound found in the orpiment and realgar experiments is most likely $\text{AsS}_3^{3-}$.

SCN$^-$ forms very rapidly from the reaction of polysulfides and thionates with cyanide (Leuthy and Bruce, 1979). McGill and others (1985) studied the reaction of cyanide with several metallic minerals and found that SCN$^-$ forms very slowly and uses only a small part of the cyanide. According to reaction (2), a small amount of $\text{H}_2\text{S}$ forms from the dissolution of $\text{As}_2\text{S}_3$. The oxidation of sulfides to sulfate proceeds through either polysulfides and (or) thionates
Figure 2. Percentage of arsenic extracted from orpiment, realgar and arsenopyrite in a 500 ppm cyanide solution.

(Boulègue, 1981). When the polysulfides or thionates form, the reaction with cyanide is very rapid. Consequently, additional orpiment or realgar dissolves. The data presented in figure 3 suggests that formation of SCN\(^-\) from cyanide and the sulfide part of the arsenic minerals is an important factor in the increasing solubility of orpiment and realgar over time. As long as free cyanide is available to react with the S released in the dissolution of the As-sulfide minerals, more and more As will eventually be dissolved.

The mechanism for dissolution of As from arsenopyrite is apparently different from that of the simple As-sulfide minerals. Both the Fe and As concentrations were uniform after about 100 hours. However, the formation of SCN\(^-\) continued to increase over time. A possible explanation is that the mineral continues to react with the cyanide solution to supply S for the formation of SCN\(^-\), but that precipitation of an As-Fe mineral of unknown composition occurs.

**SUMMARY**

As is dissolved from As-bearing minerals and gold ores by alkaline and alkaline cyanide solutions. At pH values equivalent to those found in heap-leach solutions, cyanide increases the concentration of arsenic that dissolves by a factor of 4 to 100 for various forms of As. Formation of SCN\(^-\) is likely one of the controls that affects the amount of dissolution of the As-bearing materials examined. Based on data presented above, cyanide reacts most strongly with orpiment, moderately with realgar, and weakly with arsenopyrite.
REFERENCES


Figure 3. The speciation of arsenic and the formation of thiocyanate from (A) orpiment, (B) realgar, and (C) arsenopyrite as a function of time.
Anaerobic Growth of Bacterial Strain Ses3 with Selenate as the Electron Acceptor

By Jodi Switzer Blum, Charles W. Culbertson, and Ronald S. Oremland

Abstract

The bacterial strain SES3 is capable of growth with selenate, nitrate, or Fe(III) as electron acceptors, and lactate as an electron donor. Selenate is reduced through selenite to elemental selenium, whereas nitrate was reduced through nitrite to ammonia, and Fe(III) was reduced to Fe(II). Lactate was oxidized to CO₂ and acetate in an approximately 1:1 ratio. Results of washed-cell experiments comparing nitrate and selenate reduction in either nitrate-grown or selenate-grown cells indicated that separate enzyme systems performed the reductions. Washcloth experiments using uniformly labelled, [U-¹⁴C] lactate, showed that fumarate, arsenate, and O₂ also functioned as electron acceptors. The respiratory inhibitors azide, carbonyl cyanide m-chlorophenyl-hydrazone (CCCP), and dinitrophenol (DNP) inhibited both selenate and nitrate reduction in washed-cell suspensions.

INTRODUCTION

Selenium, an essential micronutrient in nature, becomes toxic to plants (Aslam and others, 1990; Cappon, 1991) and animals (Nebbia and others, 1991; Van Vleet and Ferrans, 1992), and inhibitory to a variety of microorganisms (Oremland, 1993) when present at high (micromolar) concentrations. Bacterial reduction of dissolved selenium oxyanions to insoluble elemental selenium represents a potential bioremediation process (Gerhardt and others, 1991; Oremland and others, 1991; Oremland, 1993); moreover, selenate reduction in nature is a widespread phenomenon (Steinberg and Oremland, 1990). Several studies have shown that bacteria are capable of reducing selenate to elemental selenium (Oremland and others, 1989; Lortie and others, 1992; Rech and Macy, 1992; Steinberg and others, 1992; Tomei and others, 1992). A bacterium, designated strain SES3, was selectively isolated to reduce selenate. SES3 is an anaerobic, Gram negative, motile, vibroid organism that is capable of growth with selenate as the terminal electron acceptor. Strain SES3 will reduce nitrate preferentially over selenate if both are present in the growth medium (Steinberg and others, 1992). In this paper, strain SES3 is characterized with emphasis on the relation between selenate and nitrate respiration.

EXPERIMENT

Strain SES3 grew by oxidizing lactate to form acetate and CO₂ and was coupled to the reduction of either selenate (fig. 1A, B) or nitrate (fig. 2A, B). Elemental selenium was observed as a bright red precipitate in selenate reducing cultures (Steinberg and Oremland, 1990). The precipitate formation was concurrent with selenate reduction. SES3 converted approximately 6 millimoles of Fe(III) to Fe(II) concurrent with an approximately 10-fold increase in cell density (D.R. Lovely, and E.J.P. Phillips, U.S. Geological Survey, written communication, 1993). Pyruvate, or acetate +H₂ also acted as electron donors, but not acetate or H₂ alone. Experiments were performed with washed-cell suspensions to contrast the metabolism of nitrate-grown cells to selenate-grown cells. Cells of strain SES3 grown in nitrate medium were unable to use selenate unless 1 mM NO₃ was present in the cell suspension, and then only a small amount was reduced after prolonged incubation (140 hours). Selenate reduction was inhibited by 200, μg/mL chloramphenicol (50 percent inhibition). Nitrate reduction by nitrate-grown cells was rapid (2 hours) and was unaffected by chloramphenicol. Cells grown in selenate medium...
Figure 1. Growth and metabolism of strain SES3 with selenate. (A) Oxidation of lactate; and (B) Reduction of selenate; cell mass.
Figure 2. Growth and metabolism of strain SES3 with nitrate. (A) Oxidation of lactate; and (B) Reduction of nitrate; cell mass.
reduced nitrate only after prolonged incubation (160 hours) in washed-cell suspensions, and the reduction was inhibited by chloramphenicol (71 percent inhibition). The addition of 5 mM selenate to the nitrate-cell suspension accelerated nitrate reduction by selenate-grown cells (25 hours), and this reduction was inhibited by chloramphenicol (100 percent inhibition). Selenate reduction was nearly complete after 50 hours in washed-cell suspensions of selenate-grown cells with slight inhibition by chloramphenicol (13 percent inhibition). Another set of washed-cell experiments contrasted the ability of nitrate-grown and selenate-grown cells to convert [U-14C] lactate to 14CO2. Nitrate-grown cells converted 53 percent of the [U-14C] lactate to 14CO2 if NO3 was the electron acceptor, and none if SeO4 was the electron acceptor. Conversely, selenate grown cells converted 41 percent of the [U-14C] lactate to 14CO2 if SeO4 was the electron acceptor, and only 6 percent if NO3 was the electron acceptor. Both nitrate-grown and selenate-grown cells were able to couple oxidation of [U-14C] lactate to 14CO2 with reduction of arsenate, fumarate, Fe(III), and O2 (O2 was tested for NO3-grown cells only). The respiratory inhibitors azide, CCCP, and DNP were strong inhibitors of lactate oxidation for nitrate-grown, and selenate-grown cells (table 1).

### Table 1. Respiratory inhibitors; SeO4 and NO3 grown cells

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>SeO4 grown cells</th>
<th>NO3 grown cells</th>
</tr>
</thead>
<tbody>
<tr>
<td>SeO4 or NO3 control</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Rotenone (100 micromolar)</td>
<td>2.4</td>
<td>8.2</td>
</tr>
<tr>
<td>Cyanide (500 micromolar)</td>
<td>15.6</td>
<td>1.2</td>
</tr>
<tr>
<td>Azide (10 millimolar)</td>
<td>71.1</td>
<td>42.0</td>
</tr>
<tr>
<td>HOQNO (50 micromolar)</td>
<td>18.9</td>
<td>2.0</td>
</tr>
<tr>
<td>Antimycin A (100 micromolar)</td>
<td>11.0</td>
<td>20.1</td>
</tr>
<tr>
<td>CCCP (100 micromolar)</td>
<td>78.7</td>
<td>60.5</td>
</tr>
<tr>
<td>DNP (100 micromolar)</td>
<td>76.7</td>
<td>32.4</td>
</tr>
<tr>
<td>Acetone (control)</td>
<td>3.5</td>
<td>24.4</td>
</tr>
<tr>
<td>ETOH (control)</td>
<td>5.1</td>
<td>21.6</td>
</tr>
<tr>
<td>None</td>
<td>80.3</td>
<td>85.2</td>
</tr>
</tbody>
</table>

1Percent 14C recovery from added label in controls:
SeO4 grown cells = 87.8
NO3 grown cells = 89.6

CONCLUSION

Bacterial strain SES3 is potentially useful for the bioremediation of toxic selenium oxyanions. SES3 can remove selenate from solution by precipitation as elemental selenium. The presence of nitrate interferes with this process (Steinberg and others, 1992); however, washed-cell data (above) indicate that the enzyme systems for nitrate and selenate reduction function separately. Rech and Macy (1992) made similar conclusions about nitrate and selenate reduction in *Thauera selenatis*. Experiments with respiratory inhibitors indicate that nitrate and selenate reduction in strain SES3 is due to respiration.

REFERENCES


Chemical, Isotopic, and Microbiological Evidence for Denitrification During Transport of Domestic Wastewater Through a Thick Unsaturated Zone in the Mojave Desert

By Roy A. Schroeder¹, Peter Martin¹, and J.K. Bohlke²

Abstract

Septic-tank wastewater disposed in 30-foot-deep seepage pits (dry wells) at 46,000 residences is estimated to equal about 18 percent of natural recharge to the sole-source aquifer beneath the upper Mojave River Basin, which is rapidly becoming urbanized, in the high desert northeast of Los Angeles. Nitrogen in the downward-infiltrating wastewaters represents a significant potential source of nitrate contamination to underlying ground water, but increases in nitrate concentration in ground water have not yet been observed. The low nitrate concentration in the ground water may be the result of lateral dispersion in the unsaturated zone, dilution below the water table, or denitrification of wastewater nitrate in the unsaturated zone.

Measured vertical rates of movement of wastewater fronts through the unsaturated zone at three newly occupied residences ranged from 0.07 to 1 foot per day. Those measurements, along with moisture-content profiles at older residences, indicate that some wastewater has reached the water table beneath communities that are older than 5 to 10 years. As wastewater percolates from seepage pits into the unsaturated zone, reduced nitrogen is converted rapidly to nitrate at shallow depths. Analyses of water extracts of soil cores and of soil moisture from suction lysimeters deep beneath seepage pits at several residences indicate that nitrate concentrations commonly decrease with depth. The largest nitrate decreases seem to coincide with increased content of fine-grained sediments or proximity to the water table. Nitrate-reducing bacteria were found in soil cores collected from two residences. Between lysimeters at 160 and 199 feet at one residence, the decrease in nitrate concentration coincided with a large increase in sulfate, decrease in alkalinity, and increase in δ¹⁵N in nitrate. Those data are consistent with denitrification by oxidation of iron sulfide to produce ferric oxides; but if such a reaction occurs, it must be in domains that are small in comparison with the sampled volumes because the waters also contain substantial quantities of dissolved oxygen. The predominantly low nitrate concentrations in the area’s ground water are consistent with the operation of a nitrogen-removal mechanism, possibly denitrification, as wastewater moves through an unsaturated zone that averages 150 feet in thickness. However, the reducing capacity of the sediments to maintain denitrification is not known.

INTRODUCTION

Septic-tank wastewater disposed in 30-foot-deep seepage pits (dry wells) at 46,000 residences in the communities of Victorville, Apple Valley, and Hesperia, is estimated to equal about 18 percent of natural recharge to the sole-source aquifer in the upper Mojave River Basin, which is rapidly becoming urbanized, in the high desert 80 miles (mi) northeast of Los Angeles (fig. 1).

The use of seepage pits in this area, instead of near-surface leach fields that are more commonly used elsewhere, is necessitated by the widespread existence of an impermeable caliche layer near the land surface. This wastewater-disposal practice has caused concern about possible contamination of the underlying aquifer, especially by nitrate. In response to that concern, the U.S. Geological Survey began a study in 1988 to

1. Measure vertical rates of wastewater movement through the unsaturated zone,
2. Determine which chemical constituents of the wastewater reach the water table, and
3. Evaluate the current and potential effects of wastewater discharge on future ground-water quality.

This paper presents a summary of results of that study, which was funded jointly by the California Regional Water Quality Control Board, Lahontan Region, and the U.S. Geological Survey (Southern California Regional Aquifer-System Analysis program and other funds).
Instrumentation at Eight Residences

Monitoring was done to follow the movement of wastewater and to detect chemical changes in the water in the unsaturated zone at eight residences (locations shown in fig. 1) chosen to represent a range in geo-hydrologic conditions, residential density, and years of seepage-pit operation. Test holes were drilled next to the seepage pits at five previously occupied residences and through the bottoms of the seepage pits at three residences that were occupied soon after completion of drilling and instrument installation in 1988 (see table 1). Cores were collected for analysis of various physical, chemical, and microbiological properties. Multiple-depth suction lysimeters were installed for water-quality sampling at all eight residences. Galvanized-steel access tubes were installed to measure changes in soil moisture by neutron logging at the three newly occupied residences and at one previously occupied residence (Cheyenne-I site).

Possible Sources of Nitrate

Downward-infiltrating domestic wastewater is considered to be the dominant potential source of nitrate contamination to ground water in the study area because

1. There are few domestic wells at which faulty well construction could allow wastewater to "short circuit" a thick unsaturated zone that ranges from less than 50 feet (ft) beneath the Mojave River to more than 400 ft in parts of Apple Valley and Hesperia;
2. Landscaping, and its accompanying use of nitrogen fertilizers, is minimal in this desert environment;
3. What little agriculture exists has always been confined to a narrow strip adjacent to the Mojave River; and

4. Although natural nitrate-rich soils are present in parts of the Mojave and Death Valley deserts, these soils generally are small in areal extent and highly localized, and none have been reported near the study area.

Observed Nitrate Concentrations in Ground Water

Nitrogen concentrations in wastewater samples from several residences averaged almost 50 milligrams per liter (mg/L), or 3,600 micromolar (μM), and the nitrogen in the wastewater was present mostly as ammonium and organic nitrogen (see table 1). Nitrogen concentrations in infiltrating wastewater sampled below seepage pits were similar (typically 20-60 mg/L), but the nitrogen in the infiltrating wastewater was present mostly as nitrate, indicating that nitrification of wastewater occurs rapidly during infiltration. Despite this large potential source of downward-moving nitrate contamination, the nitrogen concentrations (mostly as nitrate) averaged only 1.2 mg/L (90 μM) in recent samples from 20 municipal wells in the study area. Ground water sampled just below the water table at three residences and between 5 and 100 ft below the water table in multiple-depth wells at the Apple Ranches and Rincon sites (locations shown in fig. 1) also contains little nitrate.

Possible reasons for the absence of widespread nitrate contamination in the area's ground water include the following:

1. Wastewater has reached the water table but is diluted by large-scale vertical mixing in a saturated zone that is as thick as 1,000 ft.
2. Wastewater has been retained within the unsaturated zone and has not yet reached the water table.

Table 1. Characteristics of monitoring sites at eight residences in the upper Mojave River Basin
[gal/d; gallon per day; mg/L, milligram per liter; ft, foot; --, not determined]

<table>
<thead>
<tr>
<th>Site of residence</th>
<th>Year seepage pit constructed</th>
<th>Winter water usage, 1989 (gal/d)</th>
<th>Wastewater nitrogen (mg/L)</th>
<th>Depth to water table, 1989-90 (ft)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toltec</td>
<td>1988</td>
<td>388</td>
<td>--</td>
<td>220</td>
</tr>
<tr>
<td>Cheyenne-I</td>
<td>1983</td>
<td>750</td>
<td>53</td>
<td>112</td>
</tr>
<tr>
<td>Vasquez</td>
<td>1988</td>
<td>250</td>
<td>26</td>
<td>85</td>
</tr>
<tr>
<td>Chocstaw</td>
<td>1978</td>
<td>625</td>
<td>46</td>
<td>124</td>
</tr>
<tr>
<td>Little Beaver</td>
<td>1988</td>
<td>875</td>
<td>--</td>
<td>150</td>
</tr>
<tr>
<td>Kiowa</td>
<td>1979</td>
<td>812</td>
<td>22</td>
<td>150</td>
</tr>
<tr>
<td>Cheyenne-II</td>
<td>1987</td>
<td>338</td>
<td>60</td>
<td>117</td>
</tr>
<tr>
<td>Cajon</td>
<td>1977</td>
<td>260</td>
<td>40</td>
<td>252</td>
</tr>
</tbody>
</table>

1 Water table not reached by drilling; depth based on estimates from Subsurface Surveys, Inc. (1990, p. 4).
3. Nitrogen in the wastewater has been attenuated by processes such as denitrification as the wastewater moves through the unsaturated zone. Each of these explanations was evaluated in this study.

"PREDICTED" NITRATE CONCENTRATIONS IN GROUND WATER

Differences in major-ion characteristics at the Rincon multiple-depth wells indicate that vertical mixing with wastewater probably will occur within the upper 50 ft of the saturated zone. Results of simulations made using a single-cell mixing model similar to that described by Bauman and Schafer (1985) that allows nitrate from wastewater to be diluted by instantaneous vertical mixing indicate that readily measurable increases in nitrate concentration would be expected in shallow ground water within 10 years after the wastewater reaches the water table (fig. 2). The model simulates conditions that would be expected in the area between the Apple Ranchos and Rincon multiple-depth wells—a part of Apple Valley in which most of the houses were constructed in the early 1960’s and where depth to ground water is sufficiently small that wastewater should have reached the water table long ago. The absence of high nitrate concentrations in the multiple-depth wells suggests that either nitrogen is being removed from the septic-tank wastewater or the vertical mixing depth must be substantially greater than 50 ft.

RATE OF WASTEWATER MOVEMENT

The arrival of the wastewater wetting front in the unsaturated zone was recognized from (1) temporal changes in neutron-log profiles, (2) the recovery of large sample volumes from lysimeters, and (3) increased soil moisture in cores. Downward movement of the front is indicated by the differences between successive neutron logs for a recently occupied residence at Toltec (fig. 3). Lysimeters at each depth at that site yielded recoverable water only after the neutron log indicated that the wastewater wetting front had arrived. Soil-moisture contents are relatively high throughout the unsaturated zone at the established sites and indicate that the wastewater wetting front has reached the water table at most older sites.

Measured rates (from neutron-log profiles and the suction lysimeters) of vertical movement of the wastewater wetting front in the upper 100 ft ranged from 0.07 to 1.0 foot per day (ft/d) at the three newly occupied residences. These measured vertical rates correspond to travel times of several months to about 6 years after the wastewater loading:

| Wastewater loading: 175 gallons per day per residence |
| Mixing depth: 50 feet |
| Housing density: 1 per acre |
| Hydraulic conductivity: 20 feet per day |
| Hydraulic gradient: 0.0012 |
| Porosity: 0.3 |
| Initial nitrate-N: 2 milligrams per liter |

Concentration of nitrate-N in wastewater, in milligrams per liter:

- 10 milligrams per liter
- 25 milligrams per liter
- 50 milligrams per liter

**Figure 2.** Model-computed nitrate concentrations in ground water in the study area for selected nitrate-N concentrations in wastewater.
Figure 3. Temporal variation in soil-moisture content in the unsaturated zone at the Toltec site. (Shaded areas indicate moisture additions in succeeding time intervals and record the downward movement of the wastewater wetting front.

For wastewater to reach the water table at an average depth of about 150 ft (table 1). However, the vertical rates decrease with depth, possibly owing to lateral movement of the wastewater induced by stratigraphic barriers or increasing consolidation (or cementation) of the soils. Evidence for lateral movement was found in test holes drilled 25 ft from the seepage pit at the Cheyenne-I site and 50 ft from the seepage pit at the Choctaw site.

Further evidence for lateral movement can be seen from calculations of water volume potentially held within the unsaturated zone and from chemical data at the Cajon site. If the wastewater input were 260 gallons per day (gal/d) (table 1), porosity were 0.3, and depth to ground water were 250 ft, then wastewater would saturate the soil in a 5-ft cylinder directly underlying the seepage pit in less than 2 months--if there were no lateral movement. However, chemical data (table 2, mainly chloride concentrations) indicate that wastewater at the Cajon site has moved to a depth of approximately 200 ft in about 15 years. If uniform lateral movement were assumed, then wastewater would satu-
Table 2. Water-quality data from lysimeters at the Cajon residence, Hesperia, California

Specific conductance, in microsiemens per centimeter at 25° Celsius, is given as a range of values from as many as 11 samples collected November 1991–March 1993 at each depth. Isotope ratios are in permil deviation from standards (V-SMOW for O and H, air for N, Pee Dee Belemnite for C). All other constituent concentrations except pH are in \( \mu \text{M} \) (micromole per liter), and most are from single samples. If more than one sample was analyzed, the median value is given. --, no data; <, actual value is less than value shown.

<table>
<thead>
<tr>
<th>Depth below land surface, in feet</th>
<th>35</th>
<th>70</th>
<th>97.5</th>
<th>130</th>
<th>160</th>
<th>199</th>
<th>243</th>
<th>257</th>
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</thead>
<tbody>
<tr>
<td>Constituent or property</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Specific conductance</td>
<td>448-553</td>
<td>435-525</td>
<td>463-544</td>
<td>470-590</td>
<td>493-567</td>
<td>391-535</td>
<td>248-315</td>
<td>1,000-1,330</td>
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<td>Delta deuterium</td>
<td>--</td>
<td>--</td>
<td>-59.5</td>
<td>-58.0</td>
<td>-61.0</td>
<td>-59.0</td>
<td>-59.2</td>
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</tr>
<tr>
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<td>--</td>
<td>-12.40</td>
<td>--</td>
<td>-10.30</td>
<td>--</td>
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<td>Delta nitrate nitrogen-15</td>
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<td>7.8</td>
<td>7.8</td>
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<td>--</td>
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</tr>
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<td>Molecular oxygen</td>
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<td>140</td>
<td>--</td>
<td>190</td>
<td>160</td>
<td>220</td>
<td>--</td>
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<td>.04</td>
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<td>.06</td>
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<td>720</td>
<td>770</td>
<td>--</td>
<td>320</td>
<td>340</td>
<td>250</td>
<td>--</td>
</tr>
<tr>
<td>Magnesium</td>
<td>260</td>
<td>300</td>
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<td>--</td>
<td>490</td>
<td>370</td>
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</tr>
<tr>
<td>Sodium</td>
<td>2,700</td>
<td>2,100</td>
<td>2,200</td>
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<td>1,600</td>
<td>1,800</td>
<td>1,400</td>
<td>--</td>
</tr>
<tr>
<td>Potassium</td>
<td>280</td>
<td>40</td>
<td>30</td>
<td>--</td>
<td>50</td>
<td>90</td>
<td>50</td>
<td>--</td>
</tr>
<tr>
<td>Alkalinity (as CaCO(_3))^1</td>
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<td>350</td>
<td>560</td>
<td>450</td>
<td>-34</td>
<td>660</td>
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</tr>
<tr>
<td>Sulfate</td>
<td>110</td>
<td>120</td>
<td>120</td>
<td>--</td>
<td>150</td>
<td>620</td>
<td>540</td>
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</tr>
<tr>
<td>Chloride</td>
<td>1,600</td>
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<td>1,300</td>
<td>--</td>
<td>1,000</td>
<td>890</td>
<td>110</td>
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<tr>
<td>Fluoride</td>
<td>20</td>
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<td>10</td>
<td>--</td>
<td>10</td>
<td>10</td>
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</tr>
<tr>
<td>Bromide</td>
<td>.6</td>
<td>.5</td>
<td>.8</td>
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<td>.6</td>
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<td>1,300</td>
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<td>Nitrate plus nitrate</td>
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<td>1,900</td>
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<td>2,400</td>
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<tr>
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<td>10</td>
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<td>Orthophosphate</td>
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<td>&lt;1</td>
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<tr>
<td>Boron</td>
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<td>--</td>
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<td>--</td>
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<td>.02</td>
<td>&lt;.02</td>
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<td>--</td>
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<td>--</td>
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<td>--</td>
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<td>--</td>
<td>.04</td>
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<td>.02</td>
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<td>.02</td>
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<td>14</td>
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<td>.7</td>
<td>--</td>
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<td>Organic carbon</td>
<td>240</td>
<td>300</td>
<td>230</td>
<td>350</td>
<td>290</td>
<td>170</td>
<td>450</td>
<td>1,200</td>
</tr>
</tbody>
</table>

^1Negative alkalinity calculated relative to a titration endpoint of pH 4.5.
rate the soil within a cylinder to a radial distance of about 30 ft after 15 years. Actual moisture content of soils in the wastewater zone is somewhat less than saturation, and some preexisting moisture is present in the soils; therefore, wastewater movement would be proportionately faster and lateral movement a little farther (it varies inversely with the square root of moisture content) than indicated by the calculations, but still much less than the average distance between seepage pits at adjacent residences.

Although wastewater has not yet reached the water table at the Cajon site, abundant soil moisture is present beneath the wastewater zone as evidenced by large sample volumes from the lysimeter at 243 ft. This might be the result of an accumulation of natural soil moisture in advance of the wastewater wetting front in a manner similar to that described by Young and others (1992). Specific-conductance measurements at the Cajon site between November 1991 and March 1993 indicate that no systematic change occurred in the chemical compositions in either the five lysimeters within the wastewater zone (above 199 ft) or the lysimeters at 243 and 257 ft that are below the wastewater zone. During the same period, the specific conductance at 199 ft increased monotonically in 11 successive samples by a total of nearly 40 percent, presumably because the wastewater was displacing some residual low-conductance and low-chloride soil moisture. The lysimeter at 257 ft has yielded very little water since 1991 when the water table dropped below this depth in response to nearby pumping and the recent drought in California.

### EVIDENCE FOR NITRATE REDUCTION IN THE UNSATURATED ZONE

The possibility that nitrate is being removed from wastewater in the unsaturated zone is indicated by decreases in nitrate concentrations with depth in deionized-water core extracts and in lysimeter samples from the Cheyenne-I site (fig. 4) and in lysimeter samples from the Cajon site (table 2). Additional evidence for nitrate reduction comes from the observation that bacteria capable of nitrate reduction are present in some of the soils. Higher numbers of nitrate-reducing bacteria and reduced nitrate concentrations seem to be associated with finer grained sediments and higher moisture contents at the Cheyenne-I site (fig. 4). The nitrate-concentration profile from lysimeter samples at the Cheyenne-I site is based on monitoring for a period of only about 1 year in 1988-89, after which the

![Figure 4](image-url). Grain-size distribution, moisture content, nitrate concentration, and nitrate-reducing bacteria counts at the Cheyenne-I site.

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**Figure 4.** Grain-size distribution, moisture content, nitrate concentration, and nitrate-reducing bacteria counts at the Cheyenne-I site.
Lysimeters were covered by a concrete driveway. The concrete was removed in the spring of 1993 and monitoring recently was resumed to ascertain if the decrease in nitrate concentration at depth that is shown in figure 4 represents transient or more permanent conditions, and to further evaluate possible reasons for the concentration profile that was observed.

If the reduced nitrate concentration at 199 ft at the Cajon site were solely the result of mixing of high-nitrate wastewater (represented by data at 160 ft) with low-nitrate residual soil moisture (represented by data at 243 ft), then the chloride data indicate that the lysimeter at 199 ft contains 88 percent wastewater. That percentage predicts that nitrate concentration should be 2,200 \( \mu \text{M} \). However, data in table 2 show that the actual nitrate concentration is only 1,600 \( \mu \text{M} \).

Isotopic evidence for denitrification is provided by the nitrogen-15 enrichment of the nitrate in a sample from the lysimeter at 199 ft in comparison with samples from the shallower lysimeters (fig. 4; table 2). The relation between the isotope ratios and nitrate concentrations is consistent with kinetic isotope fractionation during nitrate-consuming reactions with an isotope-enrichment factor of about -10 permil. That enrichment factor is within the wide range of values (approximately -30 to -5 permil) previously associated with denitrification in a variety of ground-water environments (Hubner, 1986; Mariotti and others, 1988; Bottcher and others, 1990; Schroeder and others, 1991; Smith and others, 1991). Isotope-enrichment factors at the lower end of this reported range, in this and in other studies, could indicate the influence of specific physicochemical factors on the reaction, or mixtures of unreacted and reacted waters from differing physicochemical environments (Hubner, 1986; Mariotti and others, 1988).

If waters entering the lysimeters at 160 and 199 ft were dominated by wastewater that had the same initial composition (both having high chloride concentrations, for example), then the differences between their measured compositions could be treated as coefficients in a net chemical reaction that occurs between those depths as the wastewater moves downward. If that assumption were correct, then the data in table 2 indicate that the wastewater gained approximately 470 \( \mu \text{M} \) of sulfate and 970 \( \mu \text{M} \) of hydrogen ion (including alkalinity lost to carbonic acid) while losing 900 \( \mu \text{M} \) of nitrate. If those quantities were normalized to hold chloride constant (assuming minor dilution of wastewater by low-salinity soil water, represented by data from the lysimeter at 243 ft), then the corresponding gains and losses would be approximately 550 \( \mu \text{M} \) sulfate and 980 \( \mu \text{M} \) hydrogen ion for 700 \( \mu \text{M} \) nitrate. Those coefficients and underlying assumptions have large uncertainties; nevertheless, they can be interpreted as evidence for a reaction involving denitrification by oxidation of iron sulfide (table 3, reaction 1).

Iron sulfide minerals have not been analyzed in the unsaturated-zone sediments, but they could be present in small quantities.

The data are not supportive of major reactions involving oxidation of organic carbon (reaction 4) or

### Table 3. Stoichiometries of some possible redox and precipitation reactions at the Cajon residence, Hesperia, California

<table>
<thead>
<tr>
<th>Geochemical reaction</th>
<th>Electron donors</th>
<th>Electron acceptors</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. ( 6\text{NO}_3^- + 2\text{FeS}_2 + 2\text{H}_2\text{O} \rightarrow 3\text{N}_2 + 2\text{FeOOH} + 4\text{SO}_4^{2-} + 2\text{H}^+ )</td>
<td>Fe,S</td>
<td>N</td>
</tr>
<tr>
<td>2. ( 14\text{NO}_3^- + 5\text{FeS}_2 + 4\text{H}^+ \rightarrow 7\text{N}_2 + 10\text{SO}_4^{2-} + 5\text{Fe}^{2+} + 2\text{H}_2\text{O} )</td>
<td>S</td>
<td>N</td>
</tr>
<tr>
<td>3. ( 2\text{NO}_3^- + 10\text{FeO} + 4\text{H}_2\text{O} + 2\text{H}^+ \rightarrow \text{N}_2 + 10\text{FeOOH} )</td>
<td>Fe</td>
<td>N</td>
</tr>
<tr>
<td>4. ( 4\text{NO}_3^- + 5(\text{CH}_2\text{O}) + 4\text{H}^+ \rightarrow 2\text{N}_2 + 5\text{H}_2\text{CO}_3 + 2\text{H}_2\text{O} )</td>
<td>C</td>
<td>N</td>
</tr>
<tr>
<td>5. ( 4\text{FeS}_2 + 10\text{SO}_4^{2-} + 10\text{H}_2\text{O} \rightarrow 4\text{FeOOH} + 8\text{SO}_4^{2-} + 16\text{H}^+ )</td>
<td>Fe,S</td>
<td>O</td>
</tr>
<tr>
<td>6. ( 2\text{FeS}_2 + 7\text{O}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{SO}_4^{2-} + 2\text{Fe}^{2+} + 4\text{H}^+ )</td>
<td>S</td>
<td>O</td>
</tr>
<tr>
<td>7. ( 4\text{Fe}^{2+} + \text{O}_2 + 6\text{H}_2\text{O} \rightarrow 4\text{FeOOH} + 8\text{H}^+ )</td>
<td>Fe</td>
<td>O</td>
</tr>
<tr>
<td>8. ( \text{Fe}^{2+} + 2\text{H}_2\text{O} \rightarrow \text{FeOOH} + 3\text{H}^+ )</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>
ferrous silicates or oxide minerals (reaction 3). The estimated ratios of sulfate gain to nitrate loss between 160 and 199 ft at the Cajon site (0.52 and 0.79, for raw data and chloride-normalized data, respectively) are similar to the ratio required by reaction 1 (0.67). The estimated ratios of hydrogen-ion gain to nitrate loss (1.1 and 1.4) are larger than that required by reaction 1 (0.33) and could indicate additional hydrogen-ion contributions from reactions such as 5 to 8 (table 3), if mixtures of waters from diverse soil domains were sampled.

Denitrification generally is inhibited in the presence of oxygen, whose concentration in soil-moisture samples brought to the surface by nitrogen-gas pressurization of the lysimeters ranged from 120 to 220 µM (3.7-7.1 mg/L). If denitrification occurred at the Cajon site, the presence of oxygen in the lysimeter samples indicates that it could be occurring in domains (possibly microenvironments) that are smaller than the volumes sampled by the lysimeters.

Denitrification by iron sulfide oxidation has been reported in ground waters from saturated-zone environments (Postma and others, 1991; Korom, 1992). If a reaction occurred at the Cajon site, it would be relatively deep in the unsaturated zone near the wastewater front. It is not known whether this is a stable feature controlled by the occurrence of some unique lithology or mineralogy localized in sediments at that depth, or if it is a transient feature that will move with the wastewater front and eventually allow nitrate to reach the underlying ground water. Monitoring is continuing at the Cajon residence to identify initial arrival of wastewater in the lysimeters at 243 and 257 ft and to determine if the apparent nitrate-sulfate exchange reaction observed near 199 ft is a stable phenomenon associated with the aquifer or a more transient condition associated with the advancing wastewater front.

**SUMMARY**

Physical and chemical evidence indicates that wastewater from domestic disposal systems has reached the water table beneath many of the older residences in the upper Mojave River Basin. However, any increases in ground-water nitrate concentration that might have resulted from the wastewater disposal have not yet been detected. The absence of high observed nitrate concentrations in the area’s ground water may by partly explained by the failure of recent wastewater discharge to have reached the water table, by dilution through vertical mixing within the saturated zone, and by the scarcity of monitor wells perforated solely near the water table. There also is some chemical and isotopic evidence locally for nitrification of wastewater nitrate within the unsaturated zone; however, the distribution of denitrification, and the capacities of the soils for maintaining it, are not known. Effects of wastewater on the aquifer could be detected by future monitoring in both the saturated and unsaturated zones.

**REFERENCES**


Potential Anhydrite Precipitation Associated With Deep Injection of Ground-Water Brine from Paradox Valley, Colorado

By Yousif K. Kharaka¹, William C. Evans¹, Gil Ambats¹, and James J. Thordsen¹

Abstract

Seepage and discharge of ground-water brine into the Dolores River in Paradox Valley, a collapsed diapiric salt anticline located in southwestern Colorado, increase the dissolved-solids load of the Colorado River annually by about 2.0 x 10⁸ kilograms. In order to abate this natural contamination, the U.S. Bureau of Reclamation plans to pump about 3,540 cubic meters per day of brine from 12 shallow wells located along the Dolores River. The brine, with a salinity of 250,000 mg/L, will be piped to the deepest (4.88 kilometers) injection well in the world, and injected mainly into the Mississippian Leadville Limestone.

Results of geochemical modeling indicate and water-rock experiments confirm that a huge mass of anhydrite, about 10,000 kilograms per day, likely will precipitate from this brine when heated to 120 °C at 500 bar—the temperature and pressure conditions in the Leadville aquifer. Precipitation of anhydrite could increase by a factor of two or more if the injected brine were allowed to mix with the highly incompatible formation water of the Leadville aquifer and if, as expected, the Mg in this brine dolomitizes the calcite of the aquifer. Dilution of the brine with river water, precipitation of its SO₄ and/or addition of precipitation inhibitors prior to injection are possible remedial actions.

INTRODUCTION

A 4.88-km-deep well, the deepest injection well in the world, was completed in 1987 by the U.S. Bureau of Reclamation for its Paradox Valley Unit. The well, located in southwestern Colorado (fig. 1), is intended for the disposal of 3,540 m³/d of ground water brine for a period of 100 years. The brine will be pumped from 12 shallow wells (<40 m deep) located strategically along the Dolores River as it traverses the topographically lowest part of the Paradox Valley. The cone of depression created by this pumping is expected to stop the natural seepages and discharges of brine into the Dolores River, which is a tributary of the Colorado River. The dissolved salt load of the Colorado River will be reduced annually by as much as 2.0 x 10⁸ kg from this operation (Flak and Brown, 1988).

Water and gas samples were obtained for chemical and isotope analyses from several brine wells, from two freshwater wells in Paradox Valley, from the Dolores River and from the Leadville Limestone, the primary injection zone in the deep well. In this summary, we report the results of geochemical modeling using SOLMINEQ (Kharaka and others, 1988) to simulate injecting the brine into the Leadville aquifer. These results are in general agreement with those obtained from our water-rock interaction experiments (Rosenbauer and others, 1992) and indicate that large amounts of anhydrite could precipitate in the Leadville aquifer.

REGIONAL SETTING

Paradox Valley is one of five northwestward-trending major salt anticlines located in the Canyon Lands of the Colorado Plateau in southwestern Colorado and southeastern Utah (fig. 1). Paradox Valley is about 40-km long and 3- to 5-km wide and has a relatively smooth floor that slopes gradually from both ends toward the Dolores River, which enters at about the midpoint of the valley and crosses perpendicular to its axis. The Dolores River has cut canyons about 400-m deep on both the northern and the southern flanks of Paradox Valley. The river canyons and valley flanks are

¹U.S. Geological Survey; Menlo Park, Calif.
nearly vertical, exposing brilliantly colored strata of sandstones and shales of pre-Cretaceous age. The diapiric anticline underlying Paradox Valley has about 4,000 m of relatively pure evaporites, mainly halite, and evaporite-rich shales (Flak and Brown, 1988). The halite has been leached from the upper 200 to 300 m to form the residual cap composed of highly brecciated gypsiferous shale. The evaporites are of Pennsylvanian age and belong to the Paradox Member of the Hermosa Formation (Cater, 1970). Quaternary alluvium deposits of sand, silt and gravel, less than 40-m thick, are present along Dolores River above the residual gypsiferous-shale cap.

The injection well, located about 1 km south of the Paradox Valley salt diapir and 5 km south of the brine wells, penetrates rocks that range in age from Precambrian to Triassic. The Leadville Limestone of Mississippian age, composed of 127 m of limestone and dolomite, is the primary injection zone. The dolomitized sections of the Leadville Limestone immediately underlying the karsted top interval have the greatest porosity (>5 percent) and permeability. The Precambrian basement rocks, composed of fractured granitoids and chlorite schist, are a secondary injection zone, although no significant amounts of fluid were recovered from this zone during the production tests.
The regional hydrology of this area is described in several reports, including those by Hanshaw and Hill (1969), U.S. Bureau of Reclamation (1978), and Ackerman and Rush (1984). Flow in the Dolores River is mainly from snow melt in the San Juan and La Plata Mountains and, consequently, the highest flow rates (as much as 142 m$^3$/s) are from April through June; the minimum flow rates have been increased since 1977 to about 1 to 3 m$^3$/s by discharges from the McPhee Reservoir (Stan Powers, U.S. Bureau of Reclamation, oral communication, 1993). The ground-water brine probably underlies the entire length of the Paradox Valley at varying depths. The brine surfaces along the Dolores River floodplain in two general areas from about the middle of the valley to the exit point of the river. A relatively freshwater layer (salinity <1,500 mg/L) floats on the brine, especially on the western side of the river where the thickness of this layer increases to about 30 m at a distance of 1 km from the river.

**CHEMICAL COMPOSITION OF WATER**

The chemical composition of selected water and gas samples collected from several Paradox Valley brine wells using submersible water pumps are given in tables 1 and 2, respectively. Large quantities of fluids were pumped from the wells prior to sampling and, in several wells, water samples were collected from two or three depth intervals. Gas compositions are included in this report because loss of gases, especially CO$_2$ and H$_2$S, from the brine prior to injection will modify its interactions in the aquifer.

The samples from the Leadville Limestone (table 1) were collected by use of a down-hole sampler at the conclusion of a long production test. The sampler, in the case of sample 88PVB-123, was placed 60 m above the top of the Leadville aquifer; the sample likely is a composite sample from all the three fractured zones of this aquifer. This conclusion is supported by the fact that the chemical composition of water in this sample is virtually the same as that in samples collected at the well head using a N$_2$ gas lift. Because the sampler was placed between the two lowest fractured zones of the Leadville Limestone, sample 88PVB-124 likely represents water from the deepest fracture zone of this aquifer. The field and laboratory methods used for sample treatment, storage, and analysis are generally those reported by Lico and others (1982).

Subsurface temperatures calculated from the chemical composition of water from the Leadville Limestone using Mg-Li, Si and Mg-corrected Na-K-Ca geothermometry (Kharaka and Mariner, 1989) give concordant results of 115 ± 5 °C. This value is in close agreement with measured temperatures (113-116 °C) in the Leadville aquifer, confirming that the samples were obtained from this aquifer and that the chemical and temperature data are reliable.

The waters from Paradox Valley wells are hypersaline brines that have salinities (250,000 mg/L) more than seven times that of seawater and a relatively uniform chemical composition. The brines are Na-Cl type water with high concentrations of SO$_4$, H$_2$S, K, Mg, and Ca. The waters from Leadville Limestone are also hypersaline brines of the Na-Cl type, but their salinities and SO$_4$ concentrations are lower and the Ca and Sr concentrations are much higher than those of Paradox Valley brines (table 1). The Br:Cl ratios for all these waters are very low and typical of brines that acquire their chemical composition from dissolution of halite and associated evaporites (Kharaka and others, 1987). The stable isotopes of water indicate that all the waters are of meteoric origin; tritium concentrations indicate that the brine contains modern water.

**GEOCHEMICAL MODELING**

Computer simulations were carried out using the latest version of the comprehensive geochemical code SOLMINEQ (Kharaka and others, 1988). This code is suitable for this study because it has options to compute the activity coefficients of solutes in brines using the Pitzer ion-interaction formulations (Pitzer, 1981), to perform water-rock interactions at temperatures and pressures of interest, and to investigate the consequences of mixing of two waters.

Results of these simulations show that the Paradox Valley brine is at saturation (±0.2 kcal/mol) with gypsum and calcite; and is slightly undersaturated (-0.5 kcal/mol) with halite at the aquifer temperature of about 15 °C. Because the solubilities of anhydrite (the stable form of calcium sulfate in the injection zone) and calcite decrease with increasing temperature, the brine becomes highly supersaturated with anhydrite and slightly supersaturated with calcite at 120 °C and 500 bar, the temperature and pressure conditions in the Leadville aquifer.

Precipitation of a large mass of anhydrite appears to be the main problem associated with injecting 3,540 m$^3$/d of Paradox Valley brine into the Leadville aquifer (fig. 2). There is a general agreement between
Table 1. Chemical composition of Paradox Valley waters from selected brine wells, from one freshwater well, from the Dolores River and from the injection well
[Concentrations in milligrams per liter; mV, millivolts; TDS, total dissolved solids]

<table>
<thead>
<tr>
<th>Solute</th>
<th>Well No. 2E</th>
<th>9E</th>
<th>12E</th>
<th>4E</th>
<th>8E</th>
<th>10E</th>
<th>13E</th>
<th>Freshwater well</th>
<th>Delores River</th>
<th>Injection well</th>
<th>Injection well</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>0.42</td>
<td>0.43</td>
<td>0.43</td>
<td>0.42</td>
<td>0.42</td>
<td>0.42</td>
<td>0.01</td>
<td>18.8</td>
<td>18.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>91,700</td>
<td>89,700</td>
<td>89,900</td>
<td>88,500</td>
<td>88,900</td>
<td>85,100</td>
<td>94,600</td>
<td>16.4</td>
<td>23</td>
<td>52,400</td>
<td>70,000</td>
</tr>
<tr>
<td>K</td>
<td>4,200</td>
<td>4,340</td>
<td>4,470</td>
<td>4,200</td>
<td>4,430</td>
<td>4,270</td>
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<td>2.36</td>
<td>2.0</td>
<td>1,750</td>
<td>2,100</td>
</tr>
<tr>
<td>NH₄</td>
<td>10.9</td>
<td>11.5</td>
<td>10.9</td>
<td>9.2</td>
<td>8.3</td>
<td>12.1</td>
<td>13.4</td>
<td>13.0</td>
<td>36.4</td>
<td>40.1</td>
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<tr>
<td>Mg</td>
<td>1,480</td>
<td>1,500</td>
<td>1,520</td>
<td>1,500</td>
<td>1,440</td>
<td>1,560</td>
<td>1,730</td>
<td>40.3</td>
<td>52.0</td>
<td>900</td>
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<tr>
<td>Ca</td>
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<td>1,330</td>
<td>1,380</td>
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<td>1,260</td>
<td>1,280</td>
<td>59.3</td>
<td>7,900</td>
<td>10,900</td>
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</tr>
<tr>
<td>Sr</td>
<td>26.1</td>
<td>27.1</td>
<td>25.6</td>
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<td>24.6</td>
<td>24.3</td>
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<td>Ba</td>
<td>0.12</td>
<td>0.07</td>
<td>0.05</td>
<td>0.07</td>
<td>0.05</td>
<td>0.05</td>
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<td>&lt;.02</td>
<td>5.52</td>
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<tr>
<td>Mn</td>
<td>0.57</td>
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<td>0.12</td>
<td>0.52</td>
<td>0.57</td>
<td>0.32</td>
<td>0.32</td>
<td>&lt;.002</td>
<td>&lt;.25</td>
<td>0.97</td>
<td>1.13</td>
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<td>Fe</td>
<td>0.35</td>
<td>&lt;.25</td>
<td>&lt;.25</td>
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<td>1.47</td>
<td>&lt;.25</td>
<td>&lt;.25</td>
<td>1.76</td>
<td>2.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>130,000</td>
<td>148,000</td>
<td>147,000</td>
<td>148,000</td>
<td>150,000</td>
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<td>154,000</td>
<td>17</td>
<td>12.0</td>
<td>99,600</td>
<td>132,000</td>
</tr>
<tr>
<td>Br</td>
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<td>86.2</td>
<td>83.7</td>
<td>85.0</td>
<td>83.7</td>
<td>93.5</td>
<td>0.6</td>
<td>187</td>
<td>257</td>
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</tr>
<tr>
<td>HCO₃</td>
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<td>285</td>
<td>258</td>
<td>295</td>
<td>285</td>
<td>226</td>
<td>257</td>
<td>334</td>
<td>122</td>
<td>273</td>
<td>185</td>
</tr>
<tr>
<td>SO₄</td>
<td>5,940</td>
<td>5,840</td>
<td>5,920</td>
<td>5,920</td>
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<td>5,860</td>
<td>5,970</td>
<td>47</td>
<td>112</td>
<td>726</td>
<td>454</td>
</tr>
<tr>
<td>H₂S</td>
<td>91</td>
<td>84</td>
<td>81</td>
<td>94</td>
<td>80</td>
<td>11</td>
<td>98</td>
<td></td>
<td>2.9</td>
<td></td>
<td>1.9</td>
</tr>
<tr>
<td>SiO₂</td>
<td>7.6</td>
<td>5.9</td>
<td>6.0</td>
<td>8.6</td>
<td>5.5</td>
<td>5.6</td>
<td>9.3</td>
<td>15.8</td>
<td>7.6</td>
<td>69.7</td>
<td>51.9</td>
</tr>
<tr>
<td>B</td>
<td>8.8</td>
<td>8.4</td>
<td>8.4</td>
<td>8.6</td>
<td>8.5</td>
<td>7.6</td>
<td>8.2</td>
<td>.03</td>
<td>16.8</td>
<td>19.1</td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>6.32</td>
<td>6.25</td>
<td>6.56</td>
<td>6.18</td>
<td>6.26</td>
<td>6.67</td>
<td>6.32</td>
<td>7.49</td>
<td>7.80</td>
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<td>5.42</td>
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<td>Eh(mV)</td>
<td>-415</td>
<td>-450</td>
<td>-445</td>
<td>-445</td>
<td>-53</td>
<td>-25</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>TDS</td>
<td>255,000</td>
<td>251,000</td>
<td>250,000</td>
<td>250,000</td>
<td>253,000</td>
<td>243,000</td>
<td>263,000</td>
<td>550</td>
<td>340</td>
<td>164,000</td>
<td>218,000</td>
</tr>
</tbody>
</table>
Table 2. Chemical composition of dissolved gas and total gas pressure obtained from selected samples of the Paradox Valley brine and from formation water in the Leadville Limestone
[Concentration in micromoles per kilogram of water; pressure in bars]

<table>
<thead>
<tr>
<th>Well No.</th>
<th>Sample No.</th>
<th>88PVB-8</th>
<th>88VB-9</th>
<th>88VB-11</th>
<th>88PVB-123</th>
<th>88PVB-124</th>
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<tr>
<td>Gas</td>
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<td></td>
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<tr>
<td>N₂</td>
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<td>115</td>
<td>143</td>
<td>203</td>
<td>3,230</td>
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<tr>
<td>O₂</td>
<td>.08</td>
<td>.05</td>
<td>&lt; .05</td>
<td>&lt; .05</td>
<td>223</td>
<td>148</td>
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<tr>
<td>Ar</td>
<td>5.7</td>
<td>5.7</td>
<td>7.9</td>
<td>44.2</td>
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<td>12,800</td>
<td>11,600</td>
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<td>C₂H₆</td>
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<td>H₂</td>
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<tr>
<td>H₂S</td>
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<td></td>
<td></td>
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<td>Total gas pressure</td>
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<td>31.9</td>
<td>32.3</td>
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</table>

Figure 2. Mass of anhydrite that may precipitate from subjecting 3,540 cubic meters per day of the Paradox Valley brine to difference temperatures and pressures. (Results from SOLMINEQ and experiments (Rosenbauer and others, 1992) are for a pressure of 600 bar. Data connected with solid lines were calculated from solubility parameters in Moller (1988) for a NaCl solution with an ionic strength equivalent to that of the Paradox brine.)
Figure 3. The percent amount of Dolores River water in the injection brine required to lower the saturation state of anhydrite to a value below 0 kilocalories per mole in order to prevent its precipitation in the injection aquifer. (Results are from computer simulations at 500 bar and assume no interaction with minerals in the injection zone.)

the experimental results (Rosenbauer and others, 1992) and those computed with SLMINEQ assuming equilibrium with anhydrite (fig. 2); at 120 °C and 500 bar, both indicate that about 10,000 kg/d of anhydrite may precipitate in the aquifer if there is no interaction with aquifer minerals.

Because calcite is the main mineral in the Leadville Formation, the concentrations of Mg in the injection brine are relatively high, and the thermodynamic constraints are favorable, dissolved Mg in the injection brine can react with this calcite to form dolomite. The reaction is

$$2\text{CaCO}_3(s) + \text{Mg}^{++} \rightarrow \text{CaMg(CO}_3)_2(s) + \text{Ca}^{++}.$$  \hspace{1cm} (1)

and results in release of Ca to the water in the aquifer. The added Ca will react with the aqueous SO$_4$ to form more anhydrite; the net or total reaction is

$$2\text{CaCO}_3(s) + \text{Mg}^{++} + \text{SO}_4^{--} \rightarrow \text{CaMg(CO}_3)_2(s) + \text{CaSO}_4(s).$$  \hspace{1cm} (2)

Assuming brine equilibrium with anhydrite, calcite and dolomite, computations with SLMINEQ show that ultimately a total of about 25,000 kg/d of anhydrite could precipitate in the Leadville aquifer. Our experiments (Rosenbauer and others, 1992) show dolomitization of calcite but a somewhat lower (20,000 kg/d) total anhydrite precipitated. This discrepancy likely is due to the continued disequilibrium between the solution and minerals in the experiments even after 80 days of reaction time (Rosenbauer and others, 1992, fig. 8), because of the slow kinetics of dolomitization (Morrow and Ricketts, 1988).

Computer simulations further indicate that there could be as much as a 50 percent increase in anhydrite precipitation if the injected brine were allowed to mix with the formation water. This increase could result because the two waters are highly incompatible chemically, especially with the very high SO$_4$ concentration in the brine and the very high Ca in formation water (table 1). Precipitation due to mixing, however, might be minimized by initially injecting Dolores River water or a mixture of brine and river water to obtain a buffer of compatible water between the formation water and the injected brine.

Computer simulation and water-rock interaction experiments are useful and cost-effective tools to indicate the novel chemical and hydrologic approaches necessary for the successful injection of these high-salinity brines. These tools, for example, show that a mixture of about 35 percent river water with the brine will not precipitate anhydrite in the absence of dolomitization (fig. 3); dilution with 65 to 70 percent river water would promote dolomitization (which could lead...
to increased porosity) without anhydrite precipitation. Simulations and experiments further indicate that other remedial actions to prevent precipitation of anhydrite could include precipitation of SO₄ as gypsum or barite at ground level and (or) addition of precipitation inhibitors, such as phosphonates, to the brine prior to injection (Matty and Tomson, 1988).

REFERENCES


Apparent Solute Dispersion in an Alluvial/Aquifer Stream System

By J. Jeffrey Starn

Abstract

In simulations of solute transport, the dispersion coefficient characterizes the spreading and mixing of the solute due to variations in groundwater flow velocity that are not explicitly included in the simulation. Although usually considered to be the result of variability in hydraulic conductivity, dispersion also can result from variations in the direction of groundwater flow. A computer simulation of groundwater flow and solute transport in an alluvial aquifer/stream system shows that fluctuations in river stage and subsequent changes in the direction of groundwater flow in the aquifer cause an increase in apparent dispersion. Solute plumes in an alluvial aquifer near a river move more slowly and become more dilute as a result of groundwater/surface-water interaction than if this interaction were not considered.

INTRODUCTION

Theoretical developments and carefully controlled field experiments have greatly increased knowledge of the way solutes disperse and mix with uncontaminated groundwater. Most groundwater contamination does not take place under carefully controlled conditions; however, there is still a need to predict the distribution of solute concentrations at sites of groundwater contamination. Environmental regulations often mandate the reduction of levels of contamination in an aquifer by specifying a target concentration that a remedial action must achieve. To select an appropriate remedial action, the degree to which the target concentrations will be achieved must be predicted, commonly using sparse data and simplistic models.

The amount of spreading and mixing a solute undergoes during advection (a process termed dispersion) must be specified correctly to successfully predict solute concentrations. The process of dispersion lowers the mean concentration of a solute in an aquifer and increases the area affected by the solute. In the commonly used advection/dispersion equation, dispersion is often assumed to be Fickian; that is, a constant dispersivity parameter can be used to predict solute mixing. The dispersivity parameter describes mixing due to variations in groundwater velocity at the microscopic and pore scale and is used to account for the lack of detailed information about solute mixing at this scale (Wheatcraft and Tyler, 1988). At groundwater contamination sites, however, there commonly is a lack of detailed information about the hydraulic-conductivity distribution, and the dispersivity parameter must also account for this variability. Field-scale dispersivity is constant only when a solute has passed through a sufficient volume of aquifer such that the mean hydraulic conductivity is constant.

Field-scale dispersion is usually considered to be the result of the heterogeneous nature of geologic materials (Garabedian and others, 1991). Several recent field studies have concentrated on the collection of detailed information about the distribution of aquifer properties (Mackay and others, 1986; LeBlanc and others, 1991; Rehfeldt and Gelhar, 1992). This type of investigation is impractical for most instances of groundwater contamination. The dispersivity parameter must, in fact, account for all variability at a site that is not explicitly known. Although not usually considered, this variability includes changes in the direction of the hydraulic gradient over time as well as geologic variability. Dispersion usually connotes only mixing caused by hydraulic properties of the aquifer; therefore, the combined effects of aquifer heterogeneity and unsteady groundwater flow is termed apparent dispersion (Goode and Konikow, 1990).
For an example of apparent dispersion, consider an alluvial-aquifer/stream system. Areas of industrial development commonly are located near rivers. This juxtaposition has resulted in ground-water contamination in many alluvial aquifers near surface streams. Ground water generally flows toward major streams, especially where these streams fully penetrate alluvial aquifers. When stream stage is high, the direction of ground-water flow near the stream can be reversed. The distance from the stream that water levels are affected by this reversal and the magnitude and duration of the water-level change produced in the aquifer are a function of the hydraulic properties of the aquifer and of the magnitude and duration of the fluctuation in stream stage. The change in direction of ground-water flow near the stream causes an apparent dispersion.

The purpose of this paper is not to determine the exact nature of dispersivity: this subject is the topic of a large amount of research currently taking place throughout academia and the U.S. Geological Survey. The purpose of this paper is to report the results of a preliminary study to simulate solute transport in an alluvial-aquifer/stream system in which the stream stage fluctuates periodically. The effect of different assumptions used in the model on apparent dispersion are compared by an objective measure of solute mixing. The preliminary results of this study will provide investigators with a qualitative knowledge of the role of stream-stage fluctuation in the spreading and dilution of contaminants in an alluvial-aquifer/stream system.

METHOD

Ground-water flow and solute transport are simulated by use of a three-dimensional, finite difference, method-of-characteristics computer code (Goode and Konikow, 1991). This code links a commonly used ground-water flow model code (McDonald and Harbaugh, 1988) with a method-of-characteristics (MOC) solute-transport model. The governing equation and definition of parameters for the MOC model are identical to those used by Konikow and Bredehoeft (1978). The ground-water-flow part of the code is used to generate a velocity field. The MOC modules track particles through this velocity field. Each particle is assigned a concentration based only on initial conditions. The dispersion process is simulated by a finite-difference approximation at the end of each time step that redistributes particle concentration as a function of the velocity and the dispersivity. The concentration at each node of the finite-difference grid is calculated from the particles within the cell block at the end of the dispersion process.

The conceptual model of ground-water flow is identical to that described by an analytical equation (Pinder and others, 1969). The equation represents a simplified version of the aquifer/stream system in which the aquifer properties are homogeneous, the aquifer has a finite width, and there is an instantaneous rise in river stage followed by a subsequent, delayed rise in ground-water stage. The analytical solution was used to check that the finite-difference model was specified correctly.

The boundaries of the model domain and the aquifer properties used in the model were selected so as to be similar to conditions in alluvial aquifers along the Ohio River and some of its larger tributaries. In the hypothetical aquifer, the bedrock valley wall is 2,000 ft from the stream. The aquifer is 50 ft thick and is composed mainly of sand with varying amounts of gravel. The sand is overlain and confined by a fine-grained unit composed of lacustrine clays and silts. Rises in river stage that are the result of discharges from dams upstream can be approximated by an instantaneous change in stage.

The finite-difference grid of the mathematical model is composed of 50 by 50 ft cells. The ground-water flow model grid is 40 columns by 20 rows. Solute-transport simulations are performed on a subarea 18 columns by 10 rows. The hydraulic conductivity used in the simulations is 60 ft/d, the storage coefficient is 0.01, and the porosity is 20 percent. The edge of the bedrock valley wall at the right-hand side of the model grid is modeled as a no-flow boundary to be consistent with the analytical model. River stage at the left-hand edge of the model grid is modeled as a constant-head boundary. The top and bottom edges are no-flow boundaries. Stage in the river fluctuates from 0 to 25 ft every 5 days; 40 time steps in each of 8 stress periods are simulated. Solute concentrations at the start of the simulation are zero everywhere except for a 4 by 4 cell block in which the concentration is 1.0 ppm of solute per cell. The solute is assumed to be conservative, that is, not affected by retardation, decay, biodegradation, or any of the other processes that act to reduce the mass of a contaminant in ground water.

In this simulation, vertical flow is not considered. In many places, the Ohio River fully penetrates the aquifer and vertical flow would occur during recharge from precipitation on the surface of the alluvial deposits; however, the amount of recharge to the aquifer can be
limited by fine-grained lacustrine deposits that have a much lower hydraulic conductivity than the aquifer. In this theoretical study, therefore, the flowfield is simulated in only two dimensions in a horizontal plane. Three-dimensional flow should be considered in the area near the stream; however, this is beyond the scope of this report.

The solute distribution is quantified at the end of each stress period by calculating its spatial moments. The zero, first, and second central moments describe, respectively, the mass of the solute in the system, the displacement of the center of the solute mass with respect to the origin, and the spatial covariance (\( \sigma^2 \)) of the solute mass (Fischer and others, 1979). The mass of contaminant in each cell is found by multiplying the concentration of contaminant in a cell by the volume of water stored in that cell. This method allows for the effect of fluid storage transients (Goode, 1990). The finite-difference model uses the dispersion coefficient (\( D \)), which is related to the dispersivity parameter (\( \alpha \)) by \( D = \alpha |V| \), where \( V \) is the magnitude of the velocity. The dispersivity can be obtained from the rate of change of the variance with respect to time or distance (\( x \)) by \( \alpha = \frac{1}{2} \frac{d}{dt} \sigma^2 \) and by \( \alpha = \frac{1}{2} \frac{d}{dx} \sigma^2 \). The dispersivity tensor is represented in two principal directions: longitudinal, along the \( x \) axis in the direction of flow; and transverse, along the \( y \) axis perpendicular to flow.

**PRELIMINARY RESULTS**

The hydraulic head distribution at the end of two stress periods is shown on figure 1. Line A is after an instantaneous rise in river stage and line B is after an instantaneous drop in river stage. The reversal of flow is apparent from the graph; however, the graph does not show that the change in river stage propagates a wave through the aquifer that causes a flow divide to move ahead of the wave. The rate of change of the variance of the plume over time is shown on figure 2. The final position and extent of the plume in relation to its origin is shown on figure 3.

The slopes of graphs of various \( x \)-axis and \( y \)-axis variants are listed in table 1. The slope is the rate of change of the variants. In the cases where the slope is determined with respect to distance, the slope is calculated from the data at every second stress period; otherwise, the oscillatory movement of the plume caused by the reversal of flow direction results in a slope with a low \( r^2 \). In this manner, the calculation of dispersivity is...
based on the concentration distribution after each complete cycle of flow reversal. The dispersivities and ratios of longitudinal to transverse dispersivity calculated from the rate of change of the variance and the velocity are listed in Table 2. The true dispersivities used in the simulation are 50 ft longitudinal and 5 ft transverse.

### Table 1. Parameters used to determine dispersivity

<table>
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<tr>
<th>Parameter</th>
<th>Slope</th>
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<td>distance over time</td>
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<td>y-variance over time</td>
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### Table 2. Dispersivity calculated from model results

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<th>Direction</th>
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<td>longitudinal</td>
<td>937</td>
<td>937</td>
</tr>
<tr>
<td>transverse</td>
<td>91.5</td>
<td>91.6</td>
</tr>
<tr>
<td>( l/t )</td>
<td>10.2</td>
<td>10.2</td>
</tr>
</tbody>
</table>

### CONCLUSIONS

The center of the plume has not moved in a constant direction because of the reversal in the direction of ground-water flow. The slope of distance with respect to time represents the apparent velocity of the center of the plume and not the actual velocities within the plume. There is apparent net movement toward the river because the gradients at the leading edge of the plume are steeper than at the trailing edge; this, in combination with the nonreversible spreading contrib-
No-flow boundary

EXPLANATION

- Model grid cell, 50 ft by 50 ft
- Initial solute concentration, 1.0 milligram per liter per cell
- Simulated line of equal concentration, in milligrams per liter.
  Contour interval 0.05 milligrams per liter.

Figure 3. Lines of equal concentration at the final position of the plume, 40 days after the start of simulation.

The flow system proposed in this study is simplistic. The effect of the conceptual model is to exaggerate the apparent dispersion caused by fluctuations in river stage; nonetheless, the study shows the nature of the effect of flow reversals in an aquifer near a river. In a real aquifer, fluctuations in stage would probably cause changes in flow direction that were less than 180°, as was simulated in this study. Changes in direction less than 180° would probably increase the transverse dispersivity relative to the longitudinal dispersivity.

The main result of this study is to show that a contaminant plume in an alluvial/aquifer stream system near a river moves more slowly and becomes more dilute as a result of ground-water/surface-water interaction than if steady flow were assumed. The implication of this for the remediation of ground-water contamination is that simulations based on matching the center of the plume and the dispersion assuming a steady flow system can be in error. Efforts to remediate contaminated ground water should consider the effects of unsteady flow.
REFERENCES


Measurements of Hydraulic Conductivity and Capillary Pressure under Unsaturated Conditions in a Laboratory Triaxial System

By Harold W. Olsen

Abstract

A new laboratory technique is being developed to provide media-specific measurements of hydraulic conductivity and capillary pressure under unsaturated conditions for modeling ground-water flow and contaminant transport in geologic systems. The technique is designed to test undisturbed specimens in a triaxial chamber under simulated in situ stress conditions and to provide direct and concurrent measurements of vertical hydraulic conductivity, capillary pressure, and the variation of these properties with degree of saturation. Constant-flow hydraulic-conductivity measurements are conducted by infusing and withdrawing identical flow rates at opposite ends of a specimen with a flow pump and measuring the resultant induced head difference with a differential pressure transducer. Additional transducers and flow pumps are used to (1) measure the capillary pressure and effective stress, (2) control and change the water content of the specimen during and between hydraulic conductivity measurements, and (3) control the specimen volume. This new technique avoids fundamental limitations of the methods commonly used in current practice, including (1) the need for duplicate specimens and separate equipment for laboratory measurements of hydraulic conductivity under saturated conditions and soil water retention, (2) the lack of stress or volume control for simulating in situ conditions in the pressure plate or tempe cell equipment generally used to measure soil-water-retention curves, and (3) the need for pore-size-distribution models to estimate the relationship between hydraulic conductivity and degree of saturation from soil-water-retention data.

INTRODUCTION

The variations of hydraulic conductivity (relative permeability) and capillary pressure (soil-water retention) with degree of saturation are functions needed to model ground-water flow and contaminant transport in geologic systems. In current practice, these functions for specific materials are commonly estimated from laboratory measurements of vertical hydraulic conductivity under saturated conditions together with soil-water-retention curves obtained with traditional pressure plates and tempe cells, and from theoretical pore-size-distribution models. This approach is very time consuming. It also has limitations that introduce uncertainties in the significance of the results. In a pressure plate or a tempe cell, an unconfined test specimen is mounted on a high-air-entry porous plate inside a chamber that can be pressurized; the porous plate is connected to a flow-rate-measuring device, such as a capillary tube or beaker, outside the chamber. A soil-water-retention curve is obtained by elevating the chamber air pressure in steps and measuring the increments of pore fluid expelled through the high-air-entry plate and into the external flow-rate-measuring device. The test is time consuming because a substantial time interval is needed to expel the pore fluid following each loading step. The specimen cannot be maintained under simulated in situ stress conditions because it is unconfined. Finally, the limitations of the pore-size-distribution models used to

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estimate relative permeabilities from soil-water-retention curves are not well understood.

This paper describes and illustrates the capabilities of a new laboratory technique for concurrent measurements of relative permeability and soil-water-retention functions on an undisturbed and unsaturated specimen that is maintained under simulated in situ stresses in a triaxial cell. This technique is an extension of recent innovations using triaxial systems for measuring vertical hydraulic conductivity under saturated conditions (Olsen and others, 1985, 1988, 1991), and the variation of capillary pressure with degree of saturation under unsaturated conditions (Znidarcic and others, 1991).

EXPERIMENTAL SYSTEM

A diagram of the experimental system is shown in figure 1. A test specimen [S] is mounted in a triaxial cell and encased in a latex membrane between 5-bar, high-air-entry, ceramic discs in the pedestal and top cap (The number "5-bar" designates the capillarity characteristics of the ceramic disc in terms of the air pressure needed to expel water from the disc). The lower ceramic disc is sealed with an O-ring in the base pedestal. The upper ceramic disc has a center hole and is sealed with two O-rings in a doughnut-shaped cavity in the top cap. A hole through the center of the top cap allows control of pore-air pressure in the specimen by an external pressure regulator [PR]. Constant-flow vertical hydraulic-conductivity measurements are performed on an unsaturated specimen by infusing and withdrawing identical flow rates at opposite ends of the specimen with a flow pump equipped with an infuse-withdraw actuator [P]. The water content of the specimen is varied by using a second flow pump [W] to infuse or withdraw water at the base of the specimen. In situ stresses on the specimen can be simulated by use of a differential pressure regulator [DPR] and a bellowfram [B] to maintain a constant pressure difference between the hydraulic chamber pressure and the pore-air pressure. Alternatively, the specimen volume can be controlled by infusing or withdrawing water into/from the triaxial chamber with a third flow pump [V] (to the extent limited by compliance of the system). One side of each of three differential pressure transducers [M, N, and Q] is connected to one of the pore-water lines feeding into the base pedestal, where the water pressure below the 5-bar ceramic disc is monitored at the base of the specimen (P_b). The other sides of these transducers monitor (1) the water pressure in the top cap above the 5-bar ceramic disc on top of the specimen [transducer M], (2) the air pressure in the center hole of the top cap that connects with the pore-air pressure at the top of the specimen [transducer Q], and (3) the chamber pressure [transducer N].

EXPERIMENTAL DATA

The capabilities of this system have been tested on an "undisturbed" sample of well-graded silty sand, 14.5 percent of which is finer than a #200 sieve, from a ground-water-recharge research site 5 km north of Golden, Colo. (Kiusalaas, 1992). Prior to mounting the specimen, the hydraulic components of the laboratory apparatus were saturated with deaired and distilled water. After mounting, the specimen was saturated by first evacuating the air in its pore space and then allowing deaired and distilled water to flow upwards through the specimen. The pore-air line at the top of the specimen was then opened to the atmosphere, and the differential pressure regulator was set to maintain the hydraulic pressure in the chamber fluid 69 kPa (10 lb/in^2) greater than the pressure in the pore-air line.

The time history of a test on the above specimen is illustrated in figures 2 and 3. ΔP_r-b is the difference between the water pressure above the ceramic disc in the top cap and the water pressure below the ceramic disc in the base pedestal. The response of this pressure difference to an externally generated flow of water through the specimen arises from resistance to water flow, both through the specimen and through the ceramic discs above and below the specimen. ΔP_a-b is the difference between the pore-air pressure at the top of the specimen and the water pressure below the porous stone in the base pedestal. When there is no flow through the system and hence no head loss through the ceramic discs, this pressure difference—called the capillary pressure, P_c—equals the pressure difference between the pore-air pressure and the pore-water pressure within the specimen. Q is the externally imposed flow rate used for making hydraulic-conductivity (k) measurements; w is the water content of the specimen in percent dry soil weight; ΔVw designates a volumetric increment of water extracted from the specimen; and P_a is the pore air pressure within the specimen.
Figure 1. Schematic diagram of a triaxial system for vertical hydraulic-conductivity and capillary-pressure measurements on an undisturbed and unsaturated specimen (S). One flow pump equipped with an infuse-withdraw actuator (P) transmits identical water flow rates to and from opposite ends of the specimen. A second flow pump equipped with a conventional syringe (W) controls the water content of the specimen. A third flow pump equipped with a conventional syringe (V) provides a means to maintain the specimen under volume control. Alternatively, the specimen can be maintained under stress control using a differential pressure regulator (DPR) and a bellowfram (B). Three transducers (M,N,&Q) monitor differences between (1) pore pressures above and below the specimen (M), (2) pore air and pore-water pressures above and below the specimen (Q), and (3) the chamber pressure and the pore-water pressure below the specimen.
Figure 2. Data obtained on a specimen mounted in the triaxial system from 0 to 300 hours (A) and from 350 to 450 hours (B) following the beginning of the test. \(P_a\) is the pore-air pressure. \(w\) is the water content in percent dry soil weight. \(\Delta P_{t-b}\) is the difference between the pore-water pressures above and below the specimen. \(\Delta P_{a-b}\) is the difference between the pore-water pressure below, and the pore-air pressure above the specimen. \(\delta V_w\) designates an increment of pore water extracted from the specimen. \(Q\) is the flow rate used to conduct a hydraulic conductivity measurement, and \(k\) is the hydraulic conductivity.
Figure 2A shows changes in pressure differences ($\Delta P_{t-b}$ and $\Delta P_{a-b}$) during the first 300 hours when the pore-air pressure ($P^a$) was maintained at atmospheric pressure. About halfway through this period, the water content of the specimen was reduced from 22.4 to 20.0 percent by extracting 2.69 cm$^3$ of pore water from the specimen. Before and after this change in water content, hydraulic conductivity measurements were conducted by generating a flow rate of $1.48 \times 10^{-5}$ cm$^3$/s through the specimen with a single-carriage flow pump equipped with an infuse-withdraw actuator. The hydraulic-conductivity values shown were calculated from the magnitudes of $\Delta P_{t-b}$ induced by the externally imposed flow rate. Because $\Delta P_{t-b}$ was measured above and below the ceramic discs in the top cap and base pedestal, respectively, it includes components of head loss in both the specimen and the ceramic discs. Note that the hydraulic conductivity did not change appreciably after reducing the water content, apparently because the magnitude of $\Delta P_{t-b}$ was dominated by resistance to flow through the ceramic discs. Low hydraulic conductivity of the ceramic discs is also indicated in the induced response of $\Delta P_{a-b}$ that parallels the induced $\Delta P_{t-b}$ during the hydraulic conductivity measurements. Between hydraulic-conductivity measurements, when there is no head loss in the ceramic discs from an externally imposed flow rate, $\Delta P_{a-b}$ equals the capillary pressure, $P_c$. Note that $P_c$ increased from nearly zero to about 6 kPa after reducing the water content from 22.4 to 20.0 percent. Finally, note that the response times for these hydraulic conductivity measurements are substantial—on the order of 20 to 30 hours.

Figure 2B shows changes in pressure differences ($\Delta P_{t-b}$ and $\Delta P_{a-b}$) during the period from 350 to 450 hours after the pore-air pressure was raised from 0 to 518 kPa while the water content was maintained constant at 20.0 percent. The first part of this time interval shows a sequence of three changes in the pressure differences resulting from the same externally-imposed flow rate, $\Delta P_{a-b}$ equals the capillary pressure, $P_c$. Note that $P_c$ increased from nearly zero to about 6 kPa after reducing the water content from 22.4 to 20.0 percent. Finally, note that the response times for these hydraulic conductivity measurements are substantial—on the order of 20 to 30 hours.

SUMMARY AND DISCUSSION

The data presented in the paper demonstrate the feasibility of concurrent measurements of constant-flow hydraulic conductivity and capillary pressure. The results depict the variation in these properties as a function of the degree of saturation for undisturbed and unsaturated soil specimens mounted in triaxial cells.
Figure 3. Data obtained on a specimen mounted in the triaxial system from 450 to 550 hours (A) and from 500 to 900 hours (B) following the beginning of the test. \( P_a \) is the pore-air pressure. \( w \) is the water content in percent dry soil weight. \( \Delta P_{t-b} \) is the difference between the pore-water pressures above and below the specimen. \( \Delta P_{a-b} \) is the difference between the pore-water pressure below, and the pore-air pressure above the specimen. \( \delta V_w \) designates an increment of pore water extracted from the specimen. \( Q \) is the flow rate used to conduct a hydraulic-conductivity measurement, and \( k \) is the hydraulic conductivity.
Figure 4. Variation of hydraulic conductivity with water content (A). Variation of capillary pressure with water content (B). Variation of response time with pore air pressure and hydraulic conductivity (C). $P_a$ is pore-air pressure in kilopascals (kPa).
The lower limit for hydraulic-conductivity measurements on unsaturated specimens is very low, in the range of $10^{10}$ cm/s. This limit is imposed by complications in the characteristics of $\Delta P_{t-b}$ that first arose between 395 and 410 hours (fig. 2B) and became more pronounced after 490 hours (fig. 3). During the hydraulic conductivity test between 395 and 410 hours, $\Delta P_{t-b}$ continued creeping upward rather than reaching a constant steady-state value. During the hydraulic conductivity tests between 490 and 505 hours, $\Delta P_{t-b}$ initially climbed at a rate that did not decrease with time and approach a steady state; however, a steady state was reached by reducing the externally-imposed flow rate by a factor of 5, from 14.8 to $2.95 \times 10^{-5}$ cm$^3$/s. This characteristic is depicted again for the hydraulic conductivity test between 630 and 720 hours. $\Delta P_{t-b}$ initially climbed at a rate that did not decrease with time toward a steady state; however, an approximate steady state was reached by reducing the externally imposed flow rate by a factor of 5—from $2.95 \times 10^{-5}$ to $5.90 \times 10^{-7}$ cm$^3$/s. Another complication in the characteristic of $\Delta P_{t-b}$ follows the hydraulic-conductivity test between 630 and 720 hours and the hydraulic-conductivity test between 810 and 860 hours. $\Delta P_{t-b}$ does not return to zero after terminating the externally imposed flow rate. A pressure difference on the order of 10 kPa persists across the specimen.

The current upper limit for hydraulic-conductivity measurements is relatively low because of the component of head loss from the ceramic discs in the measurement of hydraulic gradients induced by externally imposed flow rates through the specimen. The following approaches for minimizing or eliminating this component of head loss are currently being explored: (1) Locate and seal the sensors for measuring hydraulic heads within the ceramic discs, and do so as close as possible to the disc surfaces adjacent to the specimen; (2) replace the 1/4"-thick high-air-entry ceramic discs at the ends of the specimen with very thin high-air-entry membranes supported by high-k porous discs; and (3) mount narrow strips of high-air-entry porous fabric along the cylindrical surface of the specimen, connect these strips to access ports in the top cap and base pedestal, and use these strips as sensors for the hydraulic heads near the ends of the specimen. Because the feasibility of these approaches appears to be justified by somewhat similar applications of high-air-entry porous materials in the literature (for example, Lenhard and Parker, 1988; Oak and others, 1988; Black and Miller, 1990 and Roseberg and McCoy, 1990), we anticipate that the upper bound for constant-flow k measurements can be extended to at least $10^{-4}$ or $10^{-3}$ cm/s.

To obtain reliable values for the degree of saturation, in addition to values for water content (in percent of dry soil weight), precise control is needed for the total volume of the specimen. In the system described, the specimen volume is controlled by transmitting water to or from the triaxial chamber with a flow pump. The adequacy of this approach is being examined by evaluating the compliance of the triaxial cell and chamber fluid in response to variations in the triaxial chamber pressure and the degree of saturation of the specimen. If needed, the system will be upgraded using a more rigid test cell or a dual-cell chamber equipped with an electro-pneumatic regulator on the outer chamber that nullifies the pressure difference between the inner and outer chambers.

REFERENCES CITED


Unsaturated Zone Properties at a Hazardous-Waste-Disposal Site at the Idaho National Engineering Laboratory

By Stephanie Shakofsky and John R. Nimmo

Abstract

Field and laboratory investigations at a hazardous-waste site at the Idaho National Engineering Laboratory (INEL) have yielded measurements of the hydraulic properties that govern water and contaminant transport in the unsaturated zone. Saturated and unsaturated vertical hydraulic conductivity, soil-moisture retention, porosity, and particle-size distribution were measured in core samples collected from depths of 18 to 245 cm. In addition, the degree of soil aggregation and relative carbonate content with depth were analyzed in the field. In order to assess the effect of the disposal trenches and pits on hydrologic transport-governing properties, studies were made of (1) a simulated waste trench that was constructed as a model of the waste-containing trenches, and (2) a nearby undisturbed soil profile. Results show that the undisturbed soil profile has distinct layers whose properties differ significantly, whereas the soil profile in the simulated waste trench is, to a large degree, homogeneous. In general, the vertical movement of water is expected to be retarded in a distinctly layered medium, suggesting that the construction of trenches and pits has destroyed some natural impediments to downward flow.

INTRODUCTION

The major concern with waste isolation in shallow trenches is the infiltration of water and the eventual transport of contaminants to the ground water. Hazardous-waste sites in arid and semiarid regions are currently considered low risk because they receive little precipitation and are usually underlain by thick unsaturated zones. However, the potential for contaminant transport is always at issue and can be addressed only by a quantitative site characterization.

Knowledge of soil hydraulic properties is an essential requirement for predicting flow and contaminant transport through the unsaturated zone. A complete study involving unsaturated flow requires knowledge of the hydraulic conductivity (K) and the relation between water content (θ) and matric potential (ψ), and should include an understanding of the soil profile and any artificial disturbances of the profile. Complicating factors, such as soil layering and spatial variability, soil structure and the presence of macropores, and unstable-flow phenomena, can critically affect the fluxes of water and contaminants.

The relations among K, θ, and ψ are commonly not measured directly but are estimated by a computational procedure, such as (1) the inference of soil hydraulic parameters from empirical or theoretical relations based on particle-size or pore-size distributions, and (2) the use of measured values from presumably comparable conditions. Such estimation procedures can involve errors of an order of magnitude or more, thereby reducing their usefulness for contaminant-transport applications. For this reason, it is important to use field and laboratory techniques that directly measure the hydraulic properties with a degree of accuracy adequate for predictive modeling.

Figure 1. Map showing the Idaho National Engineering Laboratory (INEL) site, the Radioactive Waste Management Complex (RWMC), and the U.S. Geological Survey test trench area. The Subsurface Disposal Area (SDA) comprises about 60 percent of the western part of the RWMC. The simulated waste trench is a 4- by 5-meter area of the test trench area. (From Pittman, 1989, fig. 1; base from U.S. Geological Survey, 1:24,000, 1972.)
We have undertaken a study at a radioactive- and chemical-waste landfill to characterize the soil properties that govern contaminant transport in an undisturbed soil profile and in an adjacent simulated waste trench. This paper describes the methods applied and presents preliminary results of this study.

STUDY SITE

The Idaho National Engineering Laboratory (INEL) is situated on the semiarid Snake River Plain in southeastern Idaho and comprises approximately 2300 km² (fig. 1). Since 1949, INEL has produced substantial quantities of hazardous chemical and radioactive wastes, primarily associated with the development of commercial nuclear energy. Until 1970, these wastes were buried at the Subsurface Disposal Area (SDA) in trenches and pits excavated to a depth of approximately 3 to 6 m in the surficial sediments. Major constituents of the hazardous materials buried at the SDA include 334,600 L of transuranic-contaminated organic wastes, 38,600 L of acid (mostly HF and HCl), 104,500 L of sodium compounds, 88,600 L of oil, and 200 m³ of heavy metals (lead and mercury) (Laney and others, 1988). Comprehensive studies to evaluate the potential for migration of the contaminants through approximately 180 m of alternating layers of basalt and sediments into the underlying Snake River Plain aquifer have been undertaken by the Department of Energy (DOE), the U.S. Geological Survey (USGS), and other institutions.

Because hydrologic experimentation in the waste trenches and pits is potentially hazardous, the USGS, in 1986, constructed a simulated waste trench just north of the SDA boundary using the methods of waste burial historically practiced at the SDA (Davis and Pittman, 1990). This practice involves excavation of a trench to the top basalt layer (at a depth of 3-6 m), emplacement of the waste-containing barrels, and backfilling of the trench with the excavated soil. This study focuses on the simulated waste trench and the differences between properties of the trench backfill and those in the undisturbed soil adjacent to the trench.

METHODS

We used a sieve-analysis procedure to measure aggregate-size distribution and a hydrochloric acid test to determine relative carbonate content as a function of depth (Burke and others, 1986). We obtained minimally disrupted cores by use of a thin-walled, hydraulically driven sampler. Samples were collected to a depth of 245 cm from both the simulated waste trench and the adjacent undisturbed region.

Particle-size distribution was measured by an optical-scattering particle-size analyzer. Soil-moisture-retention curves were determined by use of a submersible pressure outflow cell (SPOC) (Constantz and Herkelrath, 1984), which is a modified pressure-plate assembly. Unsaturated hydraulic conductivities were estimated by the transient one-step outflow method of Gardner (1956) and Passioura (1976). Saturated hydraulic conductivity ($K_{sat}$) was measured by a falling-head method (Klute and Dirksen, 1986).

RESULTS AND DISCUSSIONS

The undisturbed soil profile description and the changes in soil properties with depth are shown in figure 2. The moisture contents indicated in figure 2 are from neutron-probe data collected at the time of sampling, by the USGS INEL Project office (John Pittman, unpublished data on file in the INEL Project office of the U.S. Geological Survey). Moisture-retention curves are shown in figure 3, and hydraulic conductivity curves are shown in figure 4.

Laboratory measurements of hydraulic properties, supported by the field data collected during sampling, demonstrate substantial differences in the properties of the trench backfill. Moisture-retention curves for the disturbed trench-soil cores are less heterogeneous vertically than the undisturbed cores; less horizontal heterogeneity also is apparent because the replicate soil samples collected from the same depths are from sites 1 to 30 m apart. The disturbed soil cores from the simulated waste trench have a greater $K_{sat}$ than adjacent undisturbed soil cores from the same depth. Particle-size analysis revealed the destruction of a high-clay-content layer, and an increase in porosity was measured in all the disturbed cores.

Considering the effects of these measured differences on the downward movement of water and contaminants, the most important factor affecting this downward movement probably is the lack of pronounced layering in the simulated waste trench. In general, the presence of layers has a retarding effect on vertical flow (Jury and others, 1991, p. 138-140). In particular, at the INEL site, the high-clay-content, low-$K_{sat}$ layer in the 130- to 170-cm depth interval in the undisturbed profile can have a significant impeding effect. If so, more water may remain above this depth.
Figure 2. Diagram of the undisturbed soil profile and changes in measured soil properties with depth in the simulated waste trench and the adjacent undisturbed soil. The increase in clay content below the 140-cm depth in the undisturbed profile correlates with increases in large aggregates and moisture content. Increases in porosity and K_s with depth are apparent in the disturbed profiles. The disruption of natural layers can be seen by the relatively smooth profiles of the aggregate distribution, clay content, and relative carbonate content in soil from the disturbed area.

Figure 3. Moisture-retention drying curves for soil samples from five depths in the simulated waste trench and from the same depths in the adjacent undisturbed area. The substantial variation of the curves for the undisturbed area is indicative of layers with distinct hydraulic properties. The curves for soils from the disturbed area show the effects of homogenization of a naturally layered soil.
interval, where evapotranspiration losses are greater, in the undisturbed than in the disturbed profile. Thus, the disturbed soil in the 3- to 6-m depth interval may be wetter and transmit more downward flow than the undisturbed soil. If these effects are substantial, then the soil-property-altering effect of trench construction is a critical element in characterizing the potential for contaminant transport.

**REFERENCES**


Fate and Transport of Atrazine at the Plains, Georgia, Ground Water Study Site

By R. A. Leonard¹, L.R. Marti¹, D.W. Hicks², and J.B. McConnell²

Abstract

Cooperative research between the U.S. Geological Survey, U.S. Department of Agriculture, Agricultural Research Service, and U.S. Environmental Protection Agency was initiated in 1986 near Plains, Georgia, to define processes that affect movement and fate of agricultural chemicals and to establish a common comprehensive data base for development and testing of mathematical models. Data from one crop cycle (mid-March 1992 to mid-March 1993) are summarized to illustrate the fate and present state of atrazine in the system after four annual treatments at normal application rates for corn. In 1992, parent atrazine dissipated in the root zone with a half-life of about 18 days. The atrazine metabolites, desethylatrazine (DEA) and desisopropylatrazine (DIA) accumulated in the root zone to a maximum 27 days after application; DEA was the primary metabolite. The maximum DEA/atrazine ratio was 0.6 40 days after atrazine application. After crop harvest in mid-July 1992, atrazine, DEA and traces of DIA were detected throughout the unsaturated zone to depths of 8.7 meters. Because the area had been treated with atrazine during the previous 3 years, the atrazine found could not be associated with a particular application. By March 1993, atrazine in the unsaturated zone had decreased from an estimated 360 grams per hectare to 100 grams per hectare. Atrazine and DEA in ground water, at the time of sampling, were at greater concentrations downgradient from the treated area, with the maximum concentrations about 60 meters downgradient from the treated plot boundary. Traces of atrazine and DEA were detected 280 meters downgradient from the plot. DEA/atrazine ratios were slightly higher in ground water compared to the unsaturated zone, possibly indicating continued transformation along the ground-water flow path.

INTRODUCTION

Detection of agricultural chemicals in ground water in many locations has established a need for research to (1) assess the severity and extent of ground-water contamination by agricultural chemicals, and (2) develop economically viable management and policy alternatives to reduce concentrations of chemicals in ground water (U.S. Department of Agriculture, 1989). In 1986, the U.S. Geological Survey; U.S. Department of Agriculture, Agricultural Research Service; U.S. Environmental Protection Agency; and the University of Georgia, began a cooperative study of chemical transport in a representative agricultural management and groundwater recharge system near Plains, Georgia. The common goal was to develop a comprehensive data base for evaluation and/or calibration of several fate and transport models. Research objectives included evaluation of (1) processes that affect fate and transport of agricultural chemicals in the soil-root, unsaturated, and saturated zones; and (2) transformation and degradation processes of selected pesticides in the respective zones.

¹U.S. Department of Agriculture, Agricultural Research Service, Southeast Watershed Research Laboratory, Tifton, Ga.
During the period 1989-91, major emphasis was placed on the movement and fate of atrazine (2-chloro-4-ethylamine-6-isopropylamino-s-triazine) and carbofuran (2,3,-dihydro-2,2-dimethyl-7-benzofuranyl methylcarbamate) in the root and upper unsaturated zones (0 - 3 m depth intervals). Results from the 1989 part of the study were summarized by Smith and Parrish (1991). Profile averaged pesticide half-life was about 15 days for atrazine and about 27 days for carbofuran. On the basis of pesticide concentrations in the soil with depth, carbofuran was more mobile than atrazine, but neither compound was detected at depths greater than 3 m. Failure to detect pesticides in ground water and in soil at depths below 3 m before mid-1991 was likely due to the fact that concentrations did not exceed detection limits of the methods in use at that time. This paper presents results of studies with atrazine conducted since 1991 using ELISA (Enzyme-linked immunosorbent assay) methods and other low-level detection methods employed in the Agricultural Research Service laboratory at Tifton, Ga. The paper describes the fate of atrazine and its state in the Plains, Ga., study after 4 years of atrazine application and examines DEA:atrazine ratios in the root, unsaturated, and saturated zones.

Atrazine is the second most widely used herbicide in the United States. Because of its widespread use, mobility, and persistence, atrazine and its metabolites have been detected in ground water more frequently than any other pesticide (Halberg, 1989). Atrazine degrades in soil to several intermediates or metabolites, some of which are relatively nonmobile (Clay and Koskinen, 1990). Metabolites resulting from dealkylation of side chains, desethylatrazine and desisopropylatrazine have properties that are similar to those of the parent atrazine. The DEA metabolite is the primary metabolite found in soils as a result of microbial degradation and in ground water (Sirons and others, 1973). The presence of DEA in relation to atrazine, particularly along paths of ground-water flow, has been examined to infer age of the contaminant or proximity to the source, assuming that DEA becomes dominant as atrazine continues to degrade over time (Leistra and Boesten, 1989; Denver and Sandstrom, 1991).

### DESCRIPTION OF STUDY AREA

The study area is in the Fall Line Hills district of the southern coastal physiographic province of southwestern Georgia in Sumter County (fig. 1A). The planted and treated area, about 0.8 ha is located at the upslope end of a 6.8-ha field of Eustis loamy sand soil (sandy, silicious thermic Psammentic Paleudult) and closely related soils. The soil is underlain by the Tallahatta Formation of the Claiborne Group, the lower portion of which is saturated (Claiborne aquifer). The saturated zone is 8.5 to 10.5 m below land surface and is 2.5 to 4.5 m thick in the study area. The Claiborne aquifer is generally unconfined and underlain by the Tuscahoma Formation of the Wilcox group which confines deeper water-bearing zones.

### METHODS

Permanent monitoring stations were located randomly at 12 sites within the treated area at the beginning of the study (fig. 1B). At each site, three 2-inch (5.1-cm) diameter wells were installed at three depth intervals in the aquifer. Results of sample collection from wells in the upper part of the aquifer are included in this report. Upgradient and downgradient monitor wells also were installed adjacent to the treated area. Vacuum lysimeters, soil-water sensors, and other instrumentation also were installed at the site (Hicks and others, 1991; Asmussen and Smith, 1991). During the period 1991-93, additional downgradient wells were installed on a line approximately parallel to the direction of the ground-water flow extending 350 m downgradient of the treated area.

Atrazine at target rates of 2.24 kg/ha was applied each spring from 1989-92 when corn (Zea Maize L.) was planted. In 1992, after atrazine application, the soil-root zone was sampled to depths of 1.5 m periodically for 63 days in seven depth increments; one core was removed each time near the center of each plot quadrant. Soil cores were collected to the top of the saturated zone in mid-July 1992 and in early March 1993. Sample segments 15 cm long were collected at midpoints of 0.08, 0.76, 1.70, 3.20, 4.70, 6.25 and 8.70 m below land surface. Atrazine, DEA, and DIA were extracted from soil samples by a 1:1 methanol:water solution.

Ground-water samples were collected periodically from monitor wells installed initially in
Figure 1A. Location of study area, planting area, and monitor sites.
Figure 1B. Location study area, planting area, and monitor sites.
and adjacent to the treated plot and from additional
downgradient wells after they were installed at later
dates. Ground-water samples were concentrated by
means of cyclohexyl solid-phase extraction columns
(SPE) with final elution in methanol. Soil extracts
were also concentrated by means of SPE columns after
methanol removal. Atrazine and its metabolites were
determined by gas chromatography using a
nitrogen:phosphorus detector and (or) high-pressure
liquid chromatography. All samples initially were
screened by use of ELISA procedures.

RESULTS AND DISCUSSION

Soil-Root Zone

Concentrations of atrazine, DEA, and DIA in
the root zone during the first 63 days after atrazine
application at corn planting in 1992 are given in table
1. Values reported are mean concentrations in four
cores, one from each plot quadrant. Based on standard
deviations (table 1), average coefficients of variation
were about 50 percent during the first 2 weeks after
application, but increased to about 100 percent at later
sampling dates as concentrations decreased. With
time, local differences in degradation and transport
rate contributes additional variation to that attributed
to application nonuniformity. Also, in the lower
concentration range, analytical precision in the
laboratory decreases. In spite of variability in the data,
initial results for recovered atrazine (2.3 kg/ha)
compares favorably with the intended application rates
of 2.2 kg/ha. On day 5, however, the 2.7 kg/ha of
atrazine recovered reflects data variability since
atrazine could not have actually increased.

During the 63-day period in 1992, atrazine
degraded to DEA, DIA and other products not
determined analytically and showed evidence of
limited vertical transport in the root zone. However,
the extent and timing of transport within and through
the root zone may be partially obscured and
confounded by several factors. Contamination of soil
layers below the surface during sampling may account
for some of the apparent changes in atrazine
concentration, particularly on the first day after
atrazine application. Atrazine transport is believed to
occur in pulses in response to rainfall and irrigation
and atrazine in these pulses may not be captured or
revealed by soil sampling, particularly if transport
occurs in preferential pathways. Vertical transport
through layered soils does not occur as a symmetrical
plume because of changes in adsorptive properties and
water-retention characteristics and with soil depth.
Evidence for downward atrazine translocation is
indicated by the relative increases in atrazine and DEA
concentrations in the 15 to 90-cm deep zone 5 to 27
days after application.

Fitting the data (table 1) to first-order kinetics
reveals a half-life of about 18 days for the parent
atrazine, similar to the half-life of 14 days found for a
1989 application to the same plot (Smith and Parrish,
1991). DEA was the dominant metabolite. The
general form of the curves (fig. 2) that show the
change in atrazine, DEA, and DIA over time is
consistent with coupled first-order reactions (Leonard
and others, 1990). The ratio of DEA to atrazine
increased to a maximum of about 0.6, 41 days after
atrazine application.

Unsaturated Zone

Soil cores were collected near sites B, C, D, F,
G, J, K, and L (fig. 1) in July 1992 after harvest of corn
silage, approximately 120 days after atrazine
application, and in February 1993. In addition to the
surface 0-15 cm interval (0.08 m midpoint), 15-cm
increments of the cores were collected with midpoints
of 0.76, 1.70, 3.20, 4.70, 6.25 and 8.70 m for atrazine
analysis. Atrazine and DEA were detected in nearly
all samples (table 2). An occasional trace of DIA near
detection limits was observed but not reported. Only
means and standard deviations are presented. Some
differences in concentration profiles were observed
that were apparently related to spatial variations in soil
and unsaturated-zone characteristics.

As expected, atrazine and DEA concentrations
were consistently higher in July 1992 than in March
1993. Concentrations were greater in the surface
horizon at both sampling times than those in lower
horizons, a result of atrazine and DEA adsorption/
binding to soil organic matter. Results obtained
represent the state of the system after 4 years of
atrazine application. Therefore, atrazine and DEA
detected can not be ascribed to a particular application.
However, comparing the July 1992 and March 1993
results indicate that atrazine and DEA were
transported from the system or degraded during the
intervening 8-month period. In contrast to the root
zone, degradation rates in the unsaturated zone may be
Table 1. Concentrations of atrazine and atrazine metabolites in the soil-root zone (0-150 cm) at different times after atrazine application to Eustis soil, at Plains, Ga., March 18, 1993

[Values are mean concentrations for four cores; value in parentheses () is standard deviation; µg/kg, micrograms per kilogram; ND, not detected]

<table>
<thead>
<tr>
<th>Days After Application</th>
<th>Depth in Soil, in Centimeters</th>
<th>Atrazine</th>
<th>Desethylatrazine (DEA)</th>
<th>Desisopropylatrazine (DIA)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0-15</td>
<td>15-30</td>
<td>30-45</td>
<td>45-60</td>
</tr>
<tr>
<td>-2</td>
<td>6.5(3.1)</td>
<td>2.6(2.1)</td>
<td>1.0(1.1)</td>
<td>0.6(1.1)</td>
</tr>
<tr>
<td>1</td>
<td>690(250)</td>
<td>49(39)</td>
<td>29(10)</td>
<td>17(9.9)</td>
</tr>
<tr>
<td>5</td>
<td>640(330)</td>
<td>270(200)</td>
<td>81(120)</td>
<td>42(69)</td>
</tr>
<tr>
<td>13</td>
<td>330(110)</td>
<td>280(180)</td>
<td>81(55)</td>
<td>61(107)</td>
</tr>
<tr>
<td>27</td>
<td>400(112)</td>
<td>201(115)</td>
<td>39(22)</td>
<td>23(23)</td>
</tr>
<tr>
<td>41</td>
<td>150(46)</td>
<td>61(24)</td>
<td>12(8.0)</td>
<td>9.6(8.6)</td>
</tr>
<tr>
<td>63</td>
<td>41(7.8)</td>
<td>43(22)</td>
<td>14(13)</td>
<td>2.0(3.9)</td>
</tr>
</tbody>
</table>

Atrazine

Desethylatrazine (DEA)

Desisopropylatrazine (DIA)
very low and ascribed mainly to chemical processes rather than biological processes.

Total mass of atrazine in the unsaturated zone was estimated using assumptions as to the depth intervals or zones represented by samples from the cores (table 2). The surface sample was assumed to represent the 0 to 0.3 m interval; while the other samples were assumed to represent equidistance intervals around the sampling point except for the 8.7-m sample which was limited to an interval of 8.5 to 9.0 m because of possible influences of the capillary fringe above the saturated zone. Using these assumptions and a value of 1.7 g/cm³ for soil bulk density, an estimate of 360 g/ha atrazine was calculated for July 1992 compared to 100 g/ha for March 1993. A mass of 100 g/ha represents about 5 percent of a single atrazine application.

Based on results given in table 2, no significant difference was found between atrazine by gas chromatography compared to atrazine by ELISA methods, although some cross-reactivity with DEA and DIA is expected in the ELISA methods. Although limited cross-reactivity has been observed, results have not been consistent. The comparisons in this report are offered only as confirmation of the presence of atrazine. The ratio of DEA to atrazine in the unsaturated zone ranged from 0.2 to 0.4 in July 1992 and from 0.3 to 1.2 in March 1993. The tendency of increased DEA:atrazine ratio after about 8 months may indicate continued degradation of atrazine.
Table 2. Atrazine and desethylatrazine (DEA) concentrations and estimated mass in the unsaturated zone at Plains, Ga., July 14, 1992, and March 10, 1993

[Depth is distance below land surface at midpoint of 15-cm core segment; values are mean concentrations of eight cores; value in parentheses ( ), standard deviation; ELISA, enzyme-linked immunosorbent assay; GC/NPD gas chromatography-nitrogen/phosphorus detector; ng/kg, micrograms per kilogram; g/ha, grams per hectare; <, less than]

<table>
<thead>
<tr>
<th>Depth in Unsaturated Zone (Meters)</th>
<th>Atrazine (ELISA) (µg/kg)</th>
<th>Atrazine GC/NPD (µg/kg)</th>
<th>DEA GC/NPD (µg/kg)</th>
<th>DEA/Atrazine Ratio</th>
<th>Estimated atrazine mass by depth interval (g/ha)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>July 1992</td>
</tr>
<tr>
<td>0.08</td>
<td>8.9 (2.2)</td>
<td>10.6 (3.8)</td>
<td>1.8 (1.2)</td>
<td>0.2</td>
<td>45</td>
</tr>
<tr>
<td>0.76</td>
<td>2.0 (1.3)</td>
<td>1.6 (1.0)</td>
<td>0.6 (0.7)</td>
<td>0.4</td>
<td>31</td>
</tr>
<tr>
<td>1.70</td>
<td>1.4 (2.1)</td>
<td>1.3 (1.8)</td>
<td>0.2 (0.4)</td>
<td>0.2</td>
<td>31</td>
</tr>
<tr>
<td>3.20</td>
<td>1.4 (2.2)</td>
<td>1.3 (1.9)</td>
<td>0.3 (0.9)</td>
<td>0.3</td>
<td>35</td>
</tr>
<tr>
<td>4.70</td>
<td>2.4 (2.2)</td>
<td>2.7 (2.1)</td>
<td>0.7 (1.3)</td>
<td>0.7</td>
<td>62</td>
</tr>
<tr>
<td>6.25</td>
<td>2.7 (3.0)</td>
<td>2.9 (3.9)</td>
<td>0.6 (.9)</td>
<td>0.6</td>
<td>140</td>
</tr>
<tr>
<td>8.70</td>
<td>2.0 (2.3)</td>
<td>2.0 (2.1)</td>
<td>.4 (.8)</td>
<td>0.4</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>360 Total</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>March 1993</td>
</tr>
<tr>
<td>0.08</td>
<td>3.1 (1.6)</td>
<td>2.8 (1.7)</td>
<td>0.8</td>
<td>0.8</td>
<td>16</td>
</tr>
<tr>
<td>0.76</td>
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<td>&lt; .1</td>
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<td>.3 (.4)</td>
<td>.3 (0.4)</td>
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<td>.4 (.6)</td>
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<tr>
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<td>.5 (.6)</td>
<td>.2 (.5)</td>
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<td>3.3 (2.5)</td>
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<tr>
<td></td>
<td></td>
<td></td>
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<td></td>
<td>100 Total</td>
</tr>
</tbody>
</table>

Saturated Zone

Atrazine was first detected in ground water in July 1991 by ELISA methods. (data not shown). Concentrations were about 1 µg/L and detected only in wells in the lower or downgradient area of the plot. Selected wells were sampled beginning in 1989. However, detection limits of the methods used at that time were insufficient for quantification at or below 1 µg/L. Also, some of the selected wells were located at upgradient sites where atrazine has not been detected to date (March, 1993). Once atrazine was detected in ground water, sampling of wells downgradient from the plot was begun. Since atrazine was found at higher concentrations in the off-plot wells, additional downgradient wells have been installed after February 1992; the latest installation in February 1993. The main line of wells extends along a north-south line through the center of the plot extending about 450 m from the northern plot boundary (fig. 1). Selected results of sampling in November 1992 and February 1993 are given in table 3. Reported concentrations are for wells along the north-south line and other wells within 15 m of the line. In November 1993, wells were not installed beyond 188 m south of the northern boundary of the plot (about 88 m beyond the plot boundary). As of April 1993, 40 wells have been installed downgradient from the plot and sampling continues. During November 1992 and February 1993, atrazine was not detected in wells on the upgradient side of the plot as expected. In November 1992, an atrazine concentration of 2.7 µg/L was detected at site J, (fig. 1), and in March, 6.6 µg/L at site F. Sites J and F are 59 and 43 m south of the northern plot boundary. Atrazine was not detected in other wells in the plot adjacent to the north-south line.
Table 3. Concentrations and ratios of atrazine and Desethylatrazine (DEA) in ground water at the Plains, Ga., Research Site  
[DEA; desethylatrazine; ND, not detected; – not analyzed; µg/L, micrograms per liter]

Approximate distance from upgradient (northern) plot boundary in meters

<table>
<thead>
<tr>
<th></th>
<th>November 1992</th>
<th>March 1993</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Atrazine</td>
<td>DEA</td>
</tr>
<tr>
<td></td>
<td>(µg/L)</td>
<td>(µg/L)</td>
</tr>
<tr>
<td>-16</td>
<td>ND</td>
<td>-</td>
</tr>
<tr>
<td>43</td>
<td>ND</td>
<td>-</td>
</tr>
<tr>
<td>59</td>
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<tr>
<td>85</td>
<td>ND</td>
<td>ND</td>
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</table>

during these two sampling periods. In both sampling periods, the maximum atrazine concentration measured in water was from wells located 155 m downgradient from the plot (table 3) -- 16.5 µg/L in November 1992, and 12.5 µg/L in March 1993. The March 1993 sampling indicated some additional downgradient transport beyond the 155 m point decreasing to about 0.2 µg/L in the 380 m well, about 280 m downgradient from the plot.

The ratio of DEA to atrazine in ground water was in the range of 0.6 to 0.9 in most wells. Occasionally ratios as high as 6 were observed, but concentrations of both atrazine and DEA were usually very low in these samples. The DEA:atrazine ratios were generally less than those reported by Denver and Sandstrom (1991); data they interpreted as suggesting continued degradation of the parent atrazine in the ground-water system. The DEA:atrazine ratios in ground-water samples from this study generally were greater, however, than found in the root and unsaturated zones.

**SUMMARY AND CONCLUSIONS**

After 4 consecutive years of atrazine application to the research plot at Plains, Ga., atrazine and atrazine metabolites are distributed throughout the hydrogeologic system, appearing at all depths sampled.
in the unsaturated zone and in ground water downgradient from the treated area. In the Eustis soil, most of the atrazine applied in 1992 dissipated from the root zone in 63 days with a half-life of about 18 days for the atrazine parent. During this time period, the atrazine metabolites DEA and DIA appeared in maximum accumulations at 27 days, DIA being minor compared to DEA. The maximum DEA:atrazine ratio in the root zone was 0.6 at 41 days.

Unsaturated-zone sampling in July 1992 and March 1993 showed that atrazine and DEA were distributed throughout the zone above the water table after atrazine application each year for 4 years. Concentrations tended to decrease downward from the surface and increase near the water table. As expected, atrazine and DEA concentrations were higher in July 1992 about 120 days after application than in March, 1993. About 260 g/ha of atrazine dissipated from the unsaturated zone between July 1992 and March 1993. The DEA:atrazine ratio in the unsaturated zone was similar to that in the root zone.

Highest concentrations of atrazine and DEA in ground water were downgradient from the plot with maximum atrazine concentrations of 12 to 16 μg/L, located about 60 meters below the lower plot boundary. The March 1993 sampling showed detectable atrazine as far as 280 meters downgradient from the plot. The DEA:atrazine ratio in ground water ranged from 0.6 to 6.0. The ratios tended to be greater in ground water than in the unsaturated zone and the maximum ratio observed in the root zone, possibly indicating continued transformations of atrazine along the flow path.

REFERENCES


Unsaturated Zone Transport at the Plains, Georgia Field Site

By D.D. Bosch\textsuperscript{1}, R.A. Leonard\textsuperscript{1}, and R.K. Hubbard\textsuperscript{1}

Abstract

Soil-water and solute-transport data have been collected over three years on a 0.81 ha field site located near Plains, Georgia. Soil cores collected from the root and vadose zone show extreme variability in movement and transport of applied bromide (Br\textsuperscript{−}) tracer. The Groundwater Loading Effects of Agricultural Management Systems - Finite Element Solute Transport (GLEAMS-FEST) root-vadose zone model was used to simulate Br\textsuperscript{−} transport below the site. Comparison of simulated concentrations to horizontally averaged profile concentrations show good agreement for year one but poor agreement thereafter, probably due to inaccurate estimates of hydraulic parameters in deeper parts of the vadose zone. Because of extreme variability in transport data, profile-averaged concentrations may not be a realistic representation of the sample data.

INTRODUCTION

In 1988, the U.S. Geological Survey, U.S. Department of Agriculture, Agricultural Research Service, U.S. Environmental Protection Agency, and University of Georgia began a cooperative study of chemical transport at an agricultural field near Plains, Georgia. Three overall objectives of the study were set: (1) identify processes that affect movement and fate of agrichemicals in the root, vadose, and saturated zones, (2) test process-based models using collected field data, and (3) use the models to evaluate the effect of agricultural-management practices on ground-water quality.

The study area is 0.81 ha and is located in the recharge area of the Claiborne aquifer system. The soil is a Eustis loamy sand (sandy, silicious thermic Psammentic Paleudult). A soil berm was constructed around the perimeter of the plot to confine runoff. A H-flume, 0.46 m (meter) height, was installed at the southwestern (SW) corner of the plot to facilitate measurement of sediment and chemical transport in the surface runoff (Smith and Parrish, 1991).

Conventional-till corn (Zea Maize L.) has been planted on the plot since 1989 (Smith and Parrish, 1991). A center-pivot irrigation system was installed to supply irrigation water to the site in order to ensure percolation of pesticides and to maintain proper soil-moisture for crop growth. The plot has been treated with the agricultural herbicides atrazine and alachlor, and with the insecticide carbofuran. A Br\textsuperscript{−} tracer was applied to the plot in 1989 and again in 1991. In addition, movement of nitrogen and chloride supplied in applied fertilizer also is being monitored. All compounds were surface-applied.

This report examines the movement of water and transport through the vadose zone following the first Br\textsuperscript{−} application. Two objectives were set for this research: (1) evaluate the variability of the Br\textsuperscript{−} plume and relate it to physical properties of the unsaturated zone and (2) examine the feasibility of modeling Br\textsuperscript{−} transport through the unsaturated zone using a one-dimensional solute-transport model.

METHODS

In 1989, Br\textsuperscript{−} was applied at a rate of 88 kg/ha on the same day corn was planted and pesticides were applied. The corn-planting date of June 13, 1989 was

\textsuperscript{1}U.S. Department of Agriculture, Agricultural Research Service, Southeast Watershed Research Laboratory, Tifton, Georgia 31793
about 70 days later than normal for southern Georgia due to difficulty instrumenting the plot.

Soil cores were collected six times after pesticide application in 1989, from 20 randomly located sites. In 1990, soil cores were collected eight times, again from 20 different sites each time. For three of these samplings, soil cores were collected down to the water table (9.1 m). Hand augers were used to collect soil-samples down to 2 m during the growing season, and a drill rig equipped with a continuous-coring device was used to collect soil cores. Continuous soil cores were collected on October 10, 1989, February 20, 1990, and November 8, 1990. These dates correspond to 120, 253, and 514 days after application, respectively. Total precipitation and irrigation falling on the plot between application and these sample dates was 80, 138, and 223 cm (centimeters), respectively.

The GLEAMS root-zone model (Leonard and others, 1987) was used to simulate the movement of Br\(^{-}\) through the root zone during 1989 and 1990. Actual precipitation and irrigation data, along with collected soil data, were used as simulation input. The FEST model (Bosch, 1989) was used to model flow through the vadose zone. The FEST model uses a linear finite element numerical solution to coupled water and solute transport. The model uses output from the GLEAMS model to provide upper boundary conditions.

Simulations were made assuming a three-layer distribution: the root zone (0 to 0.71 m), upper portion of the vadose zone (0.71 to 2.35 m), and lower vadose zone (2.35 to 5.0 m). Only the first 5 m of the profile was simulated. The rooting zone was further divided into five horizons. Hydraulic properties of each of these layers are listed in table 1. These values were based on hydraulic data determined from soil cores collected from the plot area. These soil cores were collected when the plot was established to determine texture and hydraulic properties of the root and vadose zone.

### RESULTS

**Bromide Transport**

Results of the analysis of samples collected on June 15, 1989, October 10, 1989, February 20, 1990, and November 8, 1990, are reported here. Mean Br\(^{-}\) concentrations and standard deviations of these observations for each of the sampling intervals on three of these dates are presented in figure 1. The largest concentrations of Br\(^{-}\) were observed at approximately 1.5 m on October 10, 1989, at 1.6 m on February 20, 1990, and at 2.0 m on November 8, 1990. Examination of the maximum concentrations on the three dates indicates the Br\(^{-}\) plume moved rapidly to 1.5 m, but slowly thereafter. In addition, maximum concentrations decrease with time. Large variability was observed in the Br\(^{-}\) data.

<table>
<thead>
<tr>
<th>Upper boundary (meters)</th>
<th>Lower boundary (meters)</th>
<th>Vertical saturated hydraulic conductivity (cm/hour)</th>
<th>Porosity</th>
<th>Field capacity</th>
<th>Wilting point</th>
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<td>.35</td>
<td>.33</td>
<td>.07</td>
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</table>

The Br\(^{-}\) distribution throughout the vadose zone on October 10, 1989 and November 8, 1990 was examined graphically. This examination clearly showed the Br\(^{-}\) tracer moved much deeper in the SW corner of the plot than it did in the northeastern (NE) corner. On November 8, 1990, the Br\(^{-}\) plume had moved downward to a depth of approximately 3.0 m in the SW corner, compared to 2.0 m in the NE corner. In addition, the Br\(^{-}\) distribution in the NE corner was less variable than that in the SW corner. These factors indicate a resistance to vertical transport in the NE corner between 1 and 2 m.

Soil cores collected from the plot indicate the area is underlain by unconsolidated sediments whose hydraulic characteristics are largely controlled by a clay layer extending from a depth of approximately 0.9 m to 3.4 m (Hicks and others, 1991). In the NE corner of the plot, the minimum measured vertical saturated hydraulic conductivity (Ksat) of the dense layer was 0.03 cm/hr (centimeters per hour) at 1.6 m. The layer of reduced Ksat appears to extend from 1 to 5 m in depth in the NE portion of the plot. In the SW corner, the minimum Ksat was 1.3 cm/hr at a depth of...
2.3 m. The dense layer in this corner appears to be less than 0.5 m thick. These data support the theory developed from the observed vertical distribution of Br⁻; the theory being there is greater resistance to vertical transport in the NE corner of the plot than in the SW corner.

Although not confirmed, lateral transport of Br⁻ apparently occurs along the top of the dense layer in the plot. Hicks and others (1991) reported an increase in observed Br⁻ mass in soil cores collected in the SW corner over time, but a decrease in cores collected from the NE corner. Examination of the second Br⁻ application by Hicks and others (1996) also supports this observation.

Data from the four sampling dates were separated according to quadrants from which each soil-sample was collected and a statistical comparison was made. Mean Br⁻ concentrations at each sampled depth interval in the NE and SW quadrants were statistically compared using the t test for independent sample means (Ott, 1984). Results of this comparison for the SW and NE quadrants on October 10, 1989 and November 8, 1990 are shown in Tables 2 and 3. Few of the observed differences are statistically significant at the 0.05 percent level. Data obtained from samples collected on June 15, 1989 and February 20, 1990 were similar. Because a statistical difference could not be obtained, modeling simulations were compared to data collected over the entire plot area.

### Table 2. Mean¹ in milligrams/liter and variance of the Br⁻ concentration on October 10, 1989 in the southwestern and northeastern quadrants

<table>
<thead>
<tr>
<th>Mid-point depth (meters)</th>
<th>Southwestern quadrant</th>
<th>Northeastern quadrant</th>
</tr>
</thead>
<tbody>
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<td></td>
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<td>1.8</td>
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</tr>
<tr>
<td>2.0</td>
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</tr>
<tr>
<td>2.6</td>
<td>.0a</td>
<td>.0</td>
</tr>
</tbody>
</table>

¹Means in the same row followed by the same letter are not significantly different at the 5 percent confidence level.

### Table 3. Mean¹ in milligrams/liter and variance of the Br⁻ concentration on November 8, 1990 in the southwestern and northeastern quadrants

<table>
<thead>
<tr>
<th>Mid-point depth (meters)</th>
<th>Southwestern quadrant</th>
<th>Northeastern quadrant</th>
</tr>
</thead>
<tbody>
<tr>
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<td>Mean</td>
<td>Variance</td>
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</tr>
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<td>.0</td>
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</tbody>
</table>

¹Means in the same row followed by the same letter are not significantly different at the 5 percent confidence level.
Figure 2. Simulated (*) and observed mean and standard deviation of the bromide mass concentration in the root zone on June 15, 1989.

Model Simulations

Figure 2 presents a comparison of GLEAMS simulated Br\textsuperscript{−} data and Br\textsuperscript{−} data obtained from samples collected on June 15, 1989, three days after Br\textsuperscript{−} application. Between dates of application and this sampling, 4.2 cm of rainfall and irrigation water fell on the plot area. The peak simulated Br\textsuperscript{−} mass slightly lags the observed, and the GLEAMS model predicts a more diffuse Br\textsuperscript{−} plume than what was observed. However, given the variability of the data, this simulation result may be considered an acceptable representation of the Br\textsuperscript{−} distribution in the root zone.

Simulated and observed Br\textsuperscript{−} concentrations in the vadose zone on October 10, 1989 and November 8, 1990 are shown in figure 3. Simulated data closely match observed data for October 10, 1989, but the simulated plume for November 8, 1990 is much deeper than the observed. This is due to two factors. First, this was an attempt to simulate average Br\textsuperscript{−} transport in the plot area. Because of variability of the physical and hydraulic properties of soils in the plot area, average transport is not a good representation of the actual transport process. While it appears the mean of the observations may represent the depth of transport in the NE corner, it is not representative of transport in the SW corner. Also, in an attempt to simulate this mean behavior, average hydraulic characteristics were used. These average characteristics do not appear to yield good estimates of average Br\textsuperscript{−} concentrations.

CONCLUSIONS

Initial investigation of soils at the Plains site led researchers to believe that chemical transport at the site would primarily be vertical, with little lateral transport. The surface soil is relatively coarse textured and initially appeared to be uniform in the horizontal direction. Soil and chemical data collected at this site in 1989 and 1990 indicate this is not the case. Considerable variability has been observed in texture and soil hydraulic conductivity throughout the plot. This variability has introduced a lateral flow component into the transport process. Lateral flow appears to be induced by a layer with low hydraulic conductivity which slopes from a depth of 0.9 m in the
NE corner of the plot to a depth of 2.3 m in the SW corner. Hydraulic conductivity of the layer increases in the downslope area.

This nonhomogeneity complicates data analysis. Because flow in the plot is not strictly one-dimensional, the random sampling procedure used does not produce a clear picture of Br\(^{-}\) transport throughout the plot area. Concentration of flow due to preferential flow patterns can skew sample results. Lateral flow can cause applied chemicals to move off the plot in flow patterns not consistent with groundwater flow. This can cause randomly collected samples to miss portions of the chemical plume moving off of the plot.

Although initial analysis has shown that observed differences are statistically insignificant, mean values of Br\(^{-}\) concentrations for the entire plot do not appear to be representative of the actual physical processes occurring. A more accurate representation may be made by examining observed data in light of prior knowledge of the hydraulic characteristics of the plot.

REFERENCES


Two-Dimensional Distribution of a Bromide Tracer in the Unsaturated Zone at the Plains, Georgia, Research Site

By D.W. Hicks¹, J.B. McConnell¹, H.H. Persinger¹, J.D. Scholz¹, and R.K. Hubbard²

Abstract

A cooperative research investigation was initiated in 1986 near Plains, Georgia, by the U.S. Geological Survey; and the U.S. Department of Agriculture, Agricultural Research Service, to describe the processes that affect the movement and fate of nitrogen fertilizers; the pesticides atrazine, alachlor, and carbofuran; and a potassium bromide tracer in the plant-root, unsaturated, and saturated zones. As a result of ongoing research, in 1991 emphasis was placed on field-scale research to develop a better understanding of the physical and chemical processes that occur as water flows through variably saturated or unsaturated porous media. Data collected along a farmed, 420-foot-long transect were used to define and evaluate the factors that control the rate of movement and distribution of agricultural chemicals in the unsaturated zone. Lateral (nonvertical) migration of soil water and chemicals at the interface between permeable and less permeable material is hypothesized to account for a significant part of the dispersion of agricultural chemicals in the unsaturated zone.

Lateral flow along the interface of permeable and less permeable soil may account for the rapid fluctuations observed in matric suction and the distribution of the tracer in the unsaturated zone. For this reason, the deterministic methods that are routinely used in numerical simulation of fate and transport are not valid in the vast majority of field conditions when applied in sloping, structured, variably saturated porous media.

INTRODUCTION

Heavy use of agricultural chemicals on farmland in the southeastern United States has caused concern about the possible degradation of ground-water resources. Reconnaissance evaluations of ground-water resources in this area indicate that agricultural management practices have affected water quality; however, the geographic extent of the problem is not well known. Wells in the same hydrogeologic environment, and of similar depth and construction, commonly yield water of different water quality.

The understanding of the mechanisms affecting the fate and transport of agricultural chemicals in the environment is limited. A cooperative research investigation was initiated in 1986 near Plains, Ga., by the U.S. Geological Survey (USGS); and the U.S. Department of Agriculture, Agricultural Research Service (USDA-ARS) to (1) describe the processes that affect the movement and fate of nitrogen fertilizers and selected pesticides in the soil-root, unsaturated, and saturated zones; (2) develop linked mathematical models that describe and incorporate the process-oriented findings; and (3) evaluate the affect of agricultural management practices on the chemical quality of ground water using the mathematical models (Hicks and others, 1991a).

Physical and chemical processes that occur as water flows through variably saturated or unsaturated porous media are not well understood at the field scale.
Zaslavsky and Sinai (1981a,b) suggest that the slope of land surface has a significant effect on the magnitude of horizontal components of flow in the shallow subsurface. Bakr and others (1978) indicate that, at the field scale, the spatial variability of the hydraulic properties exerts a large influence on the fate and transport of fluids in porous media. McCord and Stephens (1987) further evaluated the effect of surficial gradient on the movement of a conservative tracer (potassium bromide) in a homogeneous, highly porous media.

Preliminary research at the Plains, Ga., site indicates that nonvertical migration of soil water and chemicals along the interface between permeable and less permeable material could account for a part of the dispersion of agricultural chemicals in the unsaturated zone (Hicks and others, 1991b). Fluid-flow paths are commonly understood to deflect as the fluid passes from a medium of one hydraulic conductivity into a medium of a different conductivity. True one-dimensional transport in the unsaturated zone is rare and can only be observed where the surface soils do not have appreciable relief, and where the porous media is vertically homogeneous. For this reason, the one-dimensional deterministic methods which assume horizontal isotropic hydraulic properties that are routinely used in numerical simulation of fate and transport in sloping, structured, variably saturated porous media might not be valid where applied in the vast majority of field situations.

As a result of research at the Plains, Ga., site (Hicks and others, 1990, 1991a,b), in 1991, new emphasis was placed on research to develop a better understanding of the processes and factors controlling the rate of movement and distribution of agricultural chemicals in the unsaturated zone. This paper presents preliminary findings from this evaluation of the temporal and spatial factors affecting the fate and transport of agricultural chemicals in the unsaturated zone.

**DESCRIPTION OF STUDY AREA**

The study area is in the Fall Line Hills district of the Coastal Plain physiographic province of southwestern Georgia in Sumter County (fig. 1). A 2-acre planting area (300 by 290.4 ft (feet)) was instrumented in an interstream area that separates two small watersheds. A drainage divide separating the watersheds passes through the northeastern corner of the planting area. Altitudes range from about 463 ft at the drainage divide, to about 456 ft in the south-southwestern part of the planting area. Interior drainage is typical of the area as a result of the slight relief and sandy, highly permeable, surface soils (fig. 1 and table 1).

The unsaturated zone, about 26 to 30 ft thick, includes the undifferentiated overburden and the upper part of the Tallahatta Formation. The lithology of the undifferentiated overburden varies areally and vertically, and generally consists of alternating and intermittent layers of sand, clayey sand, and clay. The upper part of the Tallahatta Formation is less spatially variable than the undifferentiated overburden and consists mostly of fine to coarse quartz sand. However, in the southwestern part of the planting area, a relatively thin (less than 4 in. (inches) thick), discontinuous, clay layer is present in the Tallahatta Formation at a depth of about 26 to 28 ft.

**METHOD OF STUDY**

A 420-ft-long data-collection transect was established in the planting area, extending from the northeastern part of the planting area to the southwest, to evaluate the two-dimensional rate of movement and distribution of the bromide tracer in the unsaturated zone. Twenty-two sampling sites were selected along the transect at an equidistant spacing of 20 ft. Sampling sites were numbered sequentially beginning in the northeast at site 0 through site 21 in the southwest. Site 0 and site 21 are not on the planting area. Site 0 was sampled as a control point and site 21 was not sampled during this investigation. The transect passes near existing sites D, F, J, G, and H, where data collection is ongoing and considerable data have been previously collected (fig. 1). Each of the five sites (D, F, J, G, and H) is equipped with nests of 2 in. diameter monitor wells tapping specific intervals of the saturated zone, and continuous soil-moisture monitors. Soil water is monitored using electrical, resistance-block moisture sensors that are installed from land surface to a depth of 32 ft.

Additional characterization data include bulk density, saturated vertical hydraulic conductivity, and borehole geophysical logs from selected sites (sites D, F, J, G, and H). Soil cores were collected for hydraulic characterization at five sites on the transect (sites 1, 5, 9, 13, and 19) to a depth of about 27 ft at intervals of 1 or 2 ft. Particle-size distribution analyses were conducted in the Georgia Agricultural Experiment Station, Soil Characterization Laboratory, Athens, Ga. (table 1).
Typical farming operations for a corn and wheat rotation have been conducted on the planting area since 1989. During cropping, the product manufacturer-recommended applications of fertilizers and pesticides (atrazine, alachlor, and carbofuran) were incorporated. Potassium bromide salt solution (equivalent to 186 lbs (pounds) of bromide) was applied at land surface as a conservative tracer during planting in 1989. A quantity of 300 lbs of potassium bromide salt solution (equivalent to 201 lbs of bromide) was applied during planting in 1991.

To evaluate the rate of migration and distribution of the applied chemicals, 950 soil samples were collected along the transect during seven sampling periods from April 1991 through July 1992. Samples were analyzed for soil-moisture content, chloride, nitrate, and bromide in the USGS laboratory, Atlanta, Ga. Replicate quality-assurance samples were analyzed in the Agricultural Research Service laboratory, Tifton, Ga.

RESULTS

Soil-characterization data and soil-core analyses indicate that the lithology and hydraulic characteristics of the unsaturated zone are heterogeneous and vary substantially over the transect. The northeastern part of the transect near sites 1-5, near the drainage divide, is underlain by unconsolidated sediments that are predominated by a 5 to 7 ft thick zone of dense, clayey soil that extends from a depth of about 5 to 12 ft below land surface. Silt and clay in this zone ranges from about 35 to 58 percent of the soils matrix (table 1). In this zone, the vertical saturated hydraulic conductivity ranges from 0.02 ft/d (feet per day) at a depth of about 5 ft, to 0.2 ft/d at a depth of 12 ft. The ratio of silt and clay to sand in the 5- to 12-ft depth zone progressively decreases along the transect toward the southwest. At site 13, slightly west of the center of the transect, the silt and clay ranges from about 15 to 32 percent of the
Table 1. --Particle-size distribution along transect, Plains, Georgia
[Analyses by Georgia Agricultural Experiment Station, Soil
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Table 1. --Particle-size distribution along transect, Plains, Georgia --continued
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<td>36.5</td>
<td>1.8</td>
<td>96.7</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>
The dense, clayey soils in the vicinity of site D, generally have the lowest vertical hydraulic conductivity of the soils in the study area. The relatively sandy soils downslope at sites J and H have higher permeability than soils in the upslope area near site D. Because of the soils fine texture (clayey) in the vicinity of site D, they would be expected to wet more slowly, hold moisture longer, and drain more slowly than the coarse textured (sandy) soils.
Cumulative rainfall and irrigation during February and March was about 18.7 in., which resulted in considerably different responses in the daily mean matric suction at sites D, J, and H. The observed abrupt changes in matric suction in the clayey soils near site D are somewhat anomalous (fig. 2). The daily mean matric suction at a depth of 5 ft at site D (clayey soils, low vertical hydraulic conductivity) ranged from about 31.5 to 63 in. Heavy rainfall in late February produced a noticeable increase in matric suction at site D from a prerainfall level of 31.5 in. to a postrainfall level of about 63 in. within a period of a few days. At site J (moderate vertical hydraulic conductivity), the matric suction ranged from about 51.2 to 67 in. The rainfall did not produce a rapid fluctuation in the matric suction at site J and the soils apparently did not increase in wetness significantly throughout this 2-month period. The highly permeable soils at site H apparently wetted more rapidly than at site J and D, throughout this period. The daily mean matric suction at site H ranged from 90.6 in. at the beginning of February to a minimum of about 29.5 in. at the end of March. The daily mean matric suction at sites H and J were affected slightly by the period of heavy rainfall that occurred in late February, and at site D it was affected significantly. The daily mean matric suction values are reasonable considering the significantly different hydraulic characteristics exhibited by the soils at these three sites. However, the intermittent anomalous response of the soil-water sensor at site D is not fully understood.

During the late spring and early summer in the Plains, Ga., area, the evapotranspiration rate commonly exceeds the rate of combined rainfall and irrigation. Because of the above-normal rainfall that occurred during May and June 1992, the rate of rainfall exceeded evapotranspiration during this period and the soils matrix in the planting area was much wetter than

![Figure 2. Relation of combined rainfall and irrigation, and daily mean matric suction at depth of 5 feet at sites J, H, and D during February 1 through July 18, 1992, near Plains, Ga.](image-url)
in a typical year. As a result, a cumulative rainfall of 5.3 in. that occurred June 8-14 produced a marked increase in soil water (decrease in matric suction) at a depth of 5 ft at sites D, J, and H (fig. 2). At sites J and H, the rainfall resulted in a decrease in matric suction of about 19.7 to 23.6 in., followed by slow increase as the soils slowly lost moisture. The matric suction at these sites did not return to the prerainfall level until the end of June. At site D the June 8-14 rainfall resulted in a net decline in matric suction of about 31.5 in., as would be expected. However, the soil–water sensor indicated that the soils drained rapidly at site D and returned to the prerainfall condition within a few days after the rainfall ceased, and then wetted once again (fig. 2). The low vertical hydraulic conductivity of the soil matrix (clayey soils) in the vicinity of site D would prevent the rapid rate of vertical transport necessary to produce the apparent rapid increase and decrease in soil-water content. Macropore vertical transport and lateral flow along the interface of permeable and less permeable soil could account for the apparent rapid drainage of the soils above the 5-ft moisture sensor. The anomalous changes could also have resulted from sensor malfunctions caused by changes in electrical currents. Rainstorms generally have electrical fields associated with them. If the wetting front reaching the clayey soils at site D carried a current, the electrical potential relative to ground could cause a temporary malfunction of the moisture sensor resulting in anomalous readings (R.K. Hubbard, USDA-ARS, written commun., 1993).

Soil samples were collected at 11 sites along the transect on May 16, 1991 (30 days after the second bromide application), to a depth of 10 ft below land surface to evaluate the rate of movement and the distribution of the tracer in the upper part of the unsaturated zone. The intent of this sampling was to evaluate the movement of the second bromide application (April 1991), even though remnants of the initial application remained in the unsaturated zone. The samples were analyzed for soil water, nitrate, chloride, and bromide. The results of the bromide analyses are shown as lines of equal concentration on a cross-sectional graph of the transect (fig. 3). Site 1 is in the northeastern corner of the planting area and at the northeastern end of the transect. Site 19 is at the southwestern corner of the planting area. The vertical distribution of bromide in the unsaturated zone indicates the presence of a large mass of bromide at a depth of about 5 to 6 ft in the vicinity of sites 3-9. At site 13, the top of the bromide plume (interpreted to be the 1-mg/L line) was deeper in the unsaturated zone than elsewhere in the transect. The highest concentration of bromide at this site was at a depth of about 9 ft. At sites 15-19, two zones of relatively high bromide concentrations were detected in the unsaturated zone. The deeper zone of high bromide concentration was probably a remnant from the initial application in 1989. Soil samples collected from May 16, 1991, through February 26, 1992, indicate a progressive decrease in the total bromide concentration in the unsaturated zone. The distribution of bromide concentration in the unsaturated zone on February 26, 1992, is shown in figure 4. Total bromide concentration was significantly reduced at sites 6-10, but increased at site 11. Also, the zone of highest concentrations in the area of sites 1-5 was at a depth of about 5 to 6 ft; indicating that the tracer had migrated vertically only about 1 ft over a 9-month period. During this time period, the zone of highest bromide concentration at site 13 had migrated from a depth of about 9 ft to a depth of about 12 to 14 ft below land surface. Therefore, at site 13 bromide from the 1991 application migrated at a faster rate than at the other sites and continued to be detected at the deepest point in the unsaturated zone along the transect.

**SUMMARY AND CONCLUSIONS**

A cooperative research investigation was initiated in 1986 near Plains, Ga., by the U.S. Geological Survey; and the U.S. Department of Agriculture, Agricultural Research Service to (1) describe the processes that affect the movement and fate of nitrogen fertilizers and selected pesticides in the soil-root, unsaturated, and saturated zones; (2) develop linked mathematical models that describe and incorporate the process-oriented findings; and (3) evaluate the affect of agricultural management practices on the chemical quality of ground water using the mathematical models. Physical and chemical processes that occur as water flows through variably saturated or unsaturated porous media is not well understood at the field scale. Previous research at Plains indicates that lateral (nonvertical) migration of soil water and chemicals along the interface between permeable and less permeable material could account for a part of the dispersion of agricultural chemicals in the unsaturated zone.

The study area is in the Fall Line Hills district of the Coastal Plain physiographic province of southwestern Georgia in Sumter County. A 2-acre planting area (300 by 290.4 ft) was instrumented in an interstream
area that separates two small watersheds. The unsaturated zone includes the undifferentiated overburden and the upper part of the Tallahatta Formation and is about 26 to 30 ft thick. The lithology of the undifferentiated overburden differs areally and vertically. The upper part of the Tallahatta Formation is less spatially variable than the undifferentiated overburden and in general consists of fine to coarse quartz sand.

A 420-ft-long data-collection transect was established in the planting area, extending from the northeastern part of the planting area to the southwest, to evaluate the rate of movement and two-dimensional distribution of a bromide tracer in the unsaturated zone. Twenty-two sampling sites were selected along the transect at an equidistant spacing of 20 ft. Soil water was monitored using electrical, resistance-block moisture sensors that extend from land surface to a depth of 32 ft.

Typical farming operations for a corn and wheat rotation have been conducted on the planting area since 1989. During cropping, the manufacturer recommended applications of fertilizers, pesticides (atrazine, alachlor, and carbofuran) and a conservative bromide tracer were applied at land surface. Potassium bromide salt solution (equivalent to 186 lbs of bromide) was applied as a conservative tracer during planting in 1989. A quantity of 300 lbs of potassium bromide salt solution (equivalent to 201 lbs of bromide) was applied during planting in 1991.

To evaluate the rate of migration and distribution of the applied chemicals, 950 soil samples were collected along the transect during seven sampling periods from April 1991 through July 1992. Soil-characterization data and soil-core analyses indicate that the lithology and hydraulic characteristics of the unsaturated zone are heterogeneous and differ substantially over the transect.
Figure 4. Distribution of bromide concentration in the unsaturated zone beneath transect A-A', February 26, 1992.
The northeastern part of the transect, near a drainage divide, is underlain by unconsolidated sediments that are predominated by a 5 to 7 ft thick zone of dense, clayey soil comprising about 35 to 58 percent silt and clay. In this zone, the vertical saturated hydraulic conductivity ranges from 0.02 ft/d at a depth of about 5 ft, to 0.2 ft/d at a depth of 12 ft. The ratio of silt and clay to sand in the 5- to 12-ft-depth zone progressively decreases along the transect toward the southwest. At site 13, slightly west of the center of the transect, the silt and clay comprises about 15 to 32 percent of the soil matrix, and the saturated vertical hydraulic conductivity ranges from about 0.5 to 1.0 ft/d. At site 19, at the southwestern end of the transect, the silt and clay comprises about 14 to 30 percent of the soil matrix, and the saturated vertical hydraulic conductivity ranges from 1.0 to 3.0 ft/d in the upper 12 ft of the unsaturated zone. The upper part of the Tallahatta Formation (about 17 to 27 ft below land surface), which comprises the lower part of the unsaturated zone, generally consists of clean, poorly sorted fine to coarse quartz sand, and the vertical hydraulic conductivity averages about 5.0 ft/d throughout the planting area.

As a result of the differences in hydraulic characteristics, the infiltration and moisture-holding capacities of each area of the transect differ. Daily mean matric suction, at sites D, J, and H at a depth of 5 ft below land surface for the period February 1 through July 18, 1992, indicates that the apparent energy status of the soil water varied substantially. Cumulative rainfall and irrigation during February and March was about 18.7 in., which resulted in considerably different changes in the daily mean matric suction at sites D, J, and H at a depth of 5 ft for the period.

Cumulative rainfall and irrigation during February and March was about 18.7 in. and in June was 5.3 in., which resulted in considerably different responses in the daily mean matric suction at sites D, J, and H. The observed abrupt changes in matric suction in the clayey soils near site D are somewhat anomalous. The daily mean matric suction values are reasonable considering the significantly different hydraulic characteristics exhibited by the soils at these three sites. However, the intermittent anomalous response of the soil-water sensor at site D is not fully understood. The low vertical hydraulic conductivity of the soil matrix (clayey soils) in the vicinity of site D would prevent the rapid rate of vertical transport necessary to produce the apparent rapid increase and decrease in soil-water content. Macropore vertical transport and lateral flow along the interface of permeable and less permeable soil could account for the apparent rapid drainage of the soils above the 5-ft moisture sensor. The anomalous changes could also have resulted from sensor malfunctions caused by changes in electrical currents. Rainstorms generally have electrical fields associated with them. If the wetting front reaching the clayey soils at site D carried a current, the electrical potential relative to ground could cause a temporary malfunction of the moisture sensor resulting in anomalous readings.

Soil samples were collected at 11 sites along the transect on May 16, 1991 (30 days after the second bromide application), to a depth of 10 ft below land surface. Vertical distribution of bromide in the unsaturated zone indicates that a large mass of the tracer was concentrated at a depth of about 5 to 6 ft near sites 6-10. At site 13, the upper boundary of the mappable bromide plume is deeper in the unsaturated zone than it is elsewhere in the transect. Soil samples collected from May 16, 1991, through February 26, 1992, indicate a progressive decrease in the total bromide mass in the unsaturated zone. Samples collected on February 26, 1992, indicate that the total bromide mass significantly decreased at sites 6-10 but increased at site 11.

REFERENCES


Spatial Variability of Soil Properties Affecting Chemical Transport at the Plains, Georgia, Research Site

By R. K. Hubbard\textsuperscript{1}, D. D. Bosch\textsuperscript{1}, R. A. Leonard\textsuperscript{1}, and D. W. Hicks\textsuperscript{2}

Abstract

A study was conducted on a 0.81-ha site near Plains, Georgia, to determine transport rates of water and applied agricultural chemicals to ground water in a recharge area of the Coastal Plain. As part of the study, soil cores were collected from the root and vadose zone to a depth of 914 cm (30 ft). Cores were collected from 12 locations within the site to determine spatial variability of the soil physical properties. Measurements on core samples were made of particle size distribution, vertical saturated hydraulic conductivity, bulk density, and soil moisture retention. Measured soil moisture retention was compared with soil moisture retention predicted from equations based on particle size distribution and bulk density. Analyses of the soil samples showed that the physical properties varied both vertically and laterally. The soil has a sandy texture at the surface, has increased clay content from 91 to 366 cm (3 to 12 ft) deep, and then is very sandy to a depth of 914 cm (30 ft). Laterally, the plot varies in clay content in the 91 to 366 cm (3 to 12 ft) depth interval from the east to the west side, with the northeastern corner having the highest clay content. Lower vertical saturated hydraulic conductivities and higher soil-moisture retention and bulk densities are associated with increasing clay content.

The comparisons between measured and predicted volumetric-water content show that the equations adequately predict the relative magnitude of the volumetric-water content, but that absolute predictions lack precision.

INTRODUCTION

Chemical transport to ground water is of concern both economically and environmentally. Loss of nutrients and pesticides from the root zone requires replacement by the farmer at additional cost. Agricultural chemicals in ground water are an environmental concern when concentrations exceed drinking-water standards.

The primary nutrient of concern in ground water is nitrate ($\text{NO}_3^-$-$\text{N}$). Nitrate is a soluble chemical which moves freely with water. Methemoglobinemia, or blue-baby disease, can occur in infants who drink water with $\text{NO}_3^-$-$\text{N}$ concentrations in excess of 10 mg/L (Federal Register, 1975). Nitrate concentrations greater than 10 mg/L have been documented in ground water associated with agricultural activities in a number of locations (Hubbard and Sheridan, 1989).

Pesticides are of concern in ground water primarily because of possible carcinogenic effects. As of 1986, at least 17 pesticides had been reported in ground water (Cohen and others, 1986). It is now known that intrusion of low concentrations of pesticides into ground water occurs when certain combinations of conditions coincide, as, for example, when pesticides with high mobility and relatively long half-lives are applied in aquifer recharge areas (Leonard and others, 1988).

The U.S. Geological Survey, U.S. Department of Agriculture, Agricultural Research Service, and U.S. Environmental Protection Agency initiated a

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\textsuperscript{2}U.S. Geological Survey, 3039 Amwiler Road, Atlanta, GA 30360-2824.
cooperative research investigation in 1986 to develop an effective model(s) of agrichemical transport to ground water, as well as to design and instrument a field research site to provide data necessary for the validation of the model(s). The major objectives of this investigation were to (1) describe the processes that affect the transport and fate of agrichemicals in the soil-root, unsaturated, and saturated zones; (2) develop and validate a linked model(s) that mathematically describes the process-oriented findings; and (3) use the model(s) as a tool to evaluate the effect of agricultural management practices on the chemical quality of ground water.

This paper presents information on the physical properties of a research site with emphasis on the spatial variability of particle-size distribution and saturated hydraulic conductivity. Comparisons of soil-moisture retention as measured at selected sites with those predicted by equations from Rawls and others (1983) also are presented. The equations of Rawls and others (1983) were developed from root-zone soil samples, whereas the data from Plains on which the equations were tested included samples from depths up to 914 cm (30 ft). This comparison, thus, evaluated the effectiveness of the Rawls equations on both surface and subsurface horizons of a sandy Coastal Plain soil.

**MATERIALS AND METHODS**

The initial study area selected in 1986 included the upper Ty Ty Creek tributary watershed near Plains in Sumter County, Georgia. The area occupies 2.67 km² and is typical in relief and soil properties of watersheds in the Fall Line Hills district of the Coastal Plain physiographic province of southwestern Georgia (Hicks and others, 1991a). In 1989, an area was added at the southern part of the initial study area and the scale of research was reduced. A 0.81-ha plot was selected for water and solute transport studies within this new area. The plot is located within a 6.76-ha field consisting of soil classified as Eustis sand (Psammentic Paleudult).

Twelve sites (A-L) within the plot area were selected for soil characterization (fig. 1). Three sites were located randomly within each of the four quadrants of the plot. Soil samples were collected at each site by coring with hollow-stem augering equipment. Samples were collected to a depth of 914 cm (30 ft) using 6.1 cm i.d. plastic inserts inside a soil probe contained within a hollow-stem auger. Cores were collected in sections of 91, 76 or 61 cm (3, 2.5, or 2 ft). In the laboratory, the cores were removed from the plastic sleeves and sectioned to provide subsamples for determination of vertical saturated hydraulic conductivity, particle-size distribution, soil-moisture retention, and bulk density.

A flexible-membrane permeameter (Daniel and others, 1984) was used to determine vertical saturated hydraulic conductivity on minimally disturbed core sections from the 12 sites. Particle-size analyses were done on samples from all 12 sites using the hydrometer method (Day, 1965). Soil-moisture retention from -0.01 to -1 bar was measured on selected subsamples using tempe cells (Klute, 1986; Reginato and van Bavel, 1962). Bulk-density measurements were made on the same samples used for soil-moisture retention measurements.

A comparison of measured soil-moisture retention and that predicted by equations from Rawls and others (1983) was made. Rawls presents linear regression coefficients for predicting volumetric soil-water contents at matric potentials ranging from -0.2 to -15 bars. Volumetric water content is predicted as a function of relative percentages of sand, clay, and organic matter, and bulk density.

The coefficients for predicted volumetric-moisture content at -0.20, -0.33, -0.60, and -1.00 bar matric suction were used in the linear regression equations of Rawls and others (1983) to generate values for each of the samples where moisture retention was measured. Input to the equations included measured values for percentages of sand and clay, and bulk density. Organic-matter contents were assumed to be 1.0 percent for depths of 0 to 61 cm (0 to 2 ft), 0.5 percent for depths of 61 to 152 cm (2 to 5 ft), and 0.1 percent for depths of 152 to 914 cm (5 to 30 ft). From the relation of predicted volumetric-water content to matric suction, equations for this relation were generated for each sample. Because the relation between matric potential and volumetric-water content is log-linear, a log transformation of the matric potential was used prior to generating the equations by linear regression (SAS, 1989a, 1989b). From the predictive equations, volumetric water contents at -0.01, -0.30, and -1.00 bars were calculated for each sample. The predicted values were then compared with the measured values using linear regression (SAS, 1989a, 1989b).
Figure 1. Plains, Ga., research site.
RESULTS

Samples from the 12 sites showed variability in particle-size distribution both vertically and laterally. In the vertical direction the soil is sandy near the surface, has increased clay content from approximately 91 to 366 cm (3 to 12 ft) depth and then is very sandy to a depth of 914 cm (30 ft). At some sites, narrow clay bands were observed/penetrated within the 762 to 914 cm (25 to 30 ft) depth interval. Laterally, the variability of the plot is primarily related to the percentage of clay in the 91 to 457 cm (3 to 15 ft) depth interval, and to the thickness of clayey material.

Particle-size distribution, saturated hydraulic conductivity, bulk density, and volumetric-water content at -0.01, -0.30, and -1.00 bar matric potential by depth for sites A and L are shown in tables 1 and 2. The data from these two sites (A and L) are representative of the range in properties measured at the plot. At all sites, vertical variability in particle-size distribution was primarily in the relative percentages of sand and clay; increases in clay content were offset by decreases in sand content.

At site A, the soil-surface zone contains 9.1 percent clay (table 1). From 61 to 213 cm (2 to 7 ft) depth, the clay content increases to 18 to 21 percent, and from 213 to 305 cm (7 to 10 ft) depth, the clay content ranges from 26 to 27 percent. Clay content decreases somewhat from a depth of 305 to 457 cm (10 to 15 ft) (from 21 to 12 percent) and below a depth of 457 cm (15 ft) the soil is very sandy except for a narrow clay band 762 to 792 cm (25 to 26 ft) deep.

The vertical saturated hydraulic conductivity at site A ranges from 1.79 to 5.73 cm/hr. In general, the vertical saturated hydraulic conductivity is lower in the clayey zone than it is in the underlying sandy zone. The bulk density ranges from 1.51 to 1.81 g/cm³ and is greater in the zone with the highest clay content. Soil-moisture retention at matric potentials of -0.01, -0.30, and -1.00 bar also reflects the effect of clay content. Volumetric-water content is generally higher at each matric potential from depths of 107 to 411 cm (3.5 to 13.5 ft) than in the sandier material deeper in the pedon.

Surface-soil texture at site L is similar to that at site A. At depths of 107 to 335 cm (3.5 to 11 ft), clay content averages 30 percent. In contrast, the average clay content is 22.1 percent at site A in the same depth range. Clay content decreases at site L from 335 to 457 cm (11 to 15 ft) deep and the soil is very sandy from 457 to 914 cm (15 to 30 ft) deep.

The vertical saturated hydraulic conductivity at site L is notably different from that at site A in the zone of higher clay content. The average vertical saturated hydraulic conductivities are 0.41 cm/hr at site L and 2.54 cm/hr at site A in the 107 to 366 cm (3.5 to 12 ft) depth interval. Similarly to site A, the bulk density at site L is greatest in the zone with the greatest clay content. Volumetric-water content at site L also is greatest where the clay content is the greatest.

The distributions of clay and vertical saturated hydraulic conductivities in the 30 to 61, 259 to 305, 457 to 518, and 792 to 823 cm (1 to 2, 8.5 to 10, 15 to 17, and 26 to 27 ft) depth intervals are shown in figure 2. These four depth intervals represent properties in the surface zone, zone of greatest clay content, and upper and lower zones of the 457 to 914 cm (15 to 30 ft) deep material, respectively. The greatest clay content in the 30 to 61 cm (1 to 2 ft) depth interval is in the northwestern corner of the plot. Clay content averages 10 to 12 percent elsewhere. Vertical saturated hydraulic conductivity is variable in the 30 to 61 cm (1 to 2 ft) depth interval, being lowest in the central section of the plot and increasing towards both the south and the west.

Clay content in the 259 to 305 cm (8.5 to 10 ft) depth interval varies from 38 percent in the northeastern corner to 20 percent in the southwestern corner. Ground-penetrating radar patterns of the plot which were made prior to instrumentation indicated possible differences in clay content between the eastern and western sides of the plot. Soil samples from the 12 sites clearly show that clay content is greater on the eastern than on the western side, with the northeast corner having the greatest clay content in the 91 to 366 cm (3-12 ft) depth interval. Difficulties in obtaining soil samples from the northeastern quadrant by bucket augering are indicative of the high clay content. The vertical saturated hydraulic conductivity in the 259 to 305 cm (8.5-10 ft) depth interval is lower on the east side of the plot than on the west side.

Contour plots of the clay content at depths of 457 to 518 cm (15 to 17 ft) and 792 to 823 cm (26 to 27 ft) indicate that, at these depths, the texture is relatively uniform over the plot, and the soil is very sandy. In the 457 to 518 cm (15-17 ft) depth interval, the clay content ranges from 7 to 13 percent, whereas in the 792 to 823 cm (26 to 27 ft) depth interval, the
Table 1---Physical properties of soils at Site A, Plains, Georgia
[cm, centimeters; ft, feet; cm/hr, centimeters per hour; g/cm³, grams per cubic centimeter; cm³/cm³, cubic centimeter per cubic centimeter; --, not measured]

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<th>Depth Interval (cm)</th>
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<th>Silt (percent)</th>
<th>Clay (percent)</th>
<th>Vertical saturated hydraulic conductivity (cm/hr)</th>
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<td></td>
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<td>26-27</td>
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<tr>
<td>Depth Interval (cm)</td>
<td>Depth Interval (ft)</td>
<td>Sand (percent)</td>
<td>Silt (percent)</td>
<td>Clay (percent)</td>
<td>Vertical saturated hydraulic conductivity (cm/hr)</td>
<td>Bulk density (g/cm³)</td>
<td>Volumetric water content (cm³/cm³) at:</td>
</tr>
<tr>
<td>---------------------</td>
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<td>1.73</td>
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Figure 2a. Clay content and vertical saturated hydraulic conductivity at depths of 30 to 61 centimeters (1 to 2 feet) and 259 to 305 centimeters (8.5 to 10 feet).
Figure 2b. Clay content and vertical saturated hydraulic conductivity at depths of 457 to 518 centimeters (15 to 17 feet) and 792 to 823 centimeters (26 to 27 feet).
clay content ranges from 2 to 9 percent; indicating that the sand content of the soil increases with depth in the 457 to 914 cm (15 to 30 ft) depth interval. Vertical saturated hydraulic conductivity in the 457 to 518 cm (15 to 17 ft) depth interval is lower in the northeastern quadrant than it is elsewhere in the plot. At depths of 792 to 823 cm (26 to 27 ft) the vertical saturated hydraulic conductivity ranges from 1 to more than 6 cm/hr, with the northwestern quadrant having the lowest conductivity.

Physical-property data from the plot indicate potential for variable rates of water and solute movement both vertically and laterally. Observations by Hicks and others (1991b) indicated that solutes were moving laterally through the plot from the northeast to the southwest. It would appear that solutes applied in the northeastern corner of the plot were impeded vertically by the clay layer and, thus, moved laterally towards the southwest in subsurface flow. Because the eastern side of the plot generally has higher clay content than the western side, it can be hypothesized that solutes move from the eastern side in a southwesterly direction along a series of parallel flow lines. Solutes were observed at greater depth and also in higher concentrations in the southwestern corner than in the northeastern corner of the plot.

Predicted versus measured soil-water contents at -.01, -.30, and -1.00 bar matric suction are shown in figure 3. The coefficients of determination (R^2) for the relationship between predicted and measured water content at these three matric suctions were 0.63, 0.66, and 0.61, respectively. Separation of the data according to soil depth (root zone or subsoil) or texture (sandy or clayey) did not improve the coefficients of determination. The coefficients of determination indicate that the Rawls equation is generally useful as a relative predictor, but not an absolute predictor of volumetric-water content.

CONCLUSIONS

Analyses of soil samples collected from 12 sites at the Plains, Georgia, research site showed that physical properties of the soil vary both vertically and laterally. The soil has a sandy texture at the surface, has increased clay content from 91 to 366 cm (3 to 12 ft) deep, and is then very sandy to a depth of 914 cm (30 ft). Laterally, the clay content of the plot in the 91 to 366 cm (3 to 12 ft) depth interval is variable from east to west, with the northeastern
corner having the greatest clay content. Vertical saturated hydraulic conductivity decreases and soil-moisture retention and bulk density increase with increasing clay content. Comparisons of measured volumetric-water content with those predicted by the equations of Rawls and others (1983) showed that the predictive equations were generally useful. The spatial variability in soil physical properties at the site is consistent with observed patterns of chemical movement.

REFERENCES


Modeling Statistical Relations Among Shallow Ground-Water Quality, Human Activities, Land Use, and Thickness of the Unsaturated Zone on Long Island, New York

By Paul E. Stackelberg and David A.V. Eckhardt

Abstract

Water-quality data from 90 shallow observation wells in five areas of differing land use in Nassau and Suffolk Counties were used to develop statistical models that relate shallow ground-water quality to variables representing human activities and hydrogeologic conditions. The five study areas represent the full range of land uses in the two-county area and lie along the regional ground-water divide, where ground-water has a vertically downward component and thus recharges deep zones of the aquifer system.

Maximum-likelihood logistic-regression analysis of explanatory variables that describe the degree and type of human activities and hydrogeologic conditions at the 90 well sites was used to develop statistical models that can predict the probability of the presence of contaminants in shallow ground water within the two-county area. Variables found useful for representing human activities and hydrogeologic conditions include (1) population density within a 1/2-mile radius of each well, (2) percentages of land-use categories within the same area, and (3) thickness of the unsaturated zone at each well site. One model that relates the probability of the presence of volatile organic compounds (VOC’s) at concentrations of at least 1 microgram per liter to commercial and high- and medium-density residential land was selected to illustrate model application and testing procedures. Resulting predictions were compared with an independent set of water-quality data from 378 wells in Nassau and Suffolk Counties. The comparison indicates that VOC’s are more prevalent in areas with relatively little commercial and dense residential land than predicted by data from the five study areas.

INTRODUCTION

Long Island’s aquifer system is one of 14 areas being studied as part of the U.S. Geological Survey’s Toxic Substances Hydrology Program to determine relations among the chemical quality of shallow ground water and variables that represent human activities and local hydrogeologic conditions. Long Island’s aquifer system was selected because (1) large amounts of water-quality and land-use data are available; (2) the aquifer system, which provides potable water for 2.6 million inhabitants of Nassau and Suffolk Counties, has been designated a sole-source aquifer by the U.S. Environmental Protection Agency; and (3) the aquifer is susceptible to contamination from chemicals introduced at or near the land surface because the material is highly permeable.

Recent studies on Long Island related volatile organic compound (VOC) concentrations in ground water to population density through monotonic regression of data from 903 wells in Nassau and Suffolk Counties (Eckhardt and others, 1989a). This work led to the collection, in 1987-88, of new water-quality data from a network of 90 shallow observation wells in five areas of differing land use in Nassau and Suffolk Counties. Each of the five areas was delineated to...
represent a specific predominant land use and duration of sewering in 1984; these areas are categorized as (1) suburban with long-term sewering (longer than 22 years), (2) suburban with recent sewering (less than 8 years), (3) suburban without sewering, (4) agricultural, and (5) undeveloped (fig. 1). Each area lies along the regional ground-water divide, where ground water flows vertically downward and horizontally away from the divide (fig. 1).

The potential for ground-water contamination in the two-county area was predicted through statistical models that relate the presence or absence of certain contaminants in water from the 90 shallow observation wells to selected explanatory variables that represent potential contaminant sources (Eckhardt and others, 1989b). More recent work (D.A. Eckhardt and P.E. Stackelberg, U.S. Geological Survey, written commun., 1993) has expanded on these statistical modeling efforts by (1) modeling the presence of additional contaminants, (2) incorporating additional explanatory variables, and (3) using stepwise model-building strategies.

This paper describes results of the recent statistical analyses by presenting an overview of the statistical techniques used to develop models presented herein, and selecting one model to illustrate application and testing procedures. The application presents the predicted probability of VOC presence throughout Nassau and Suffolk Counties by the selected model developed from data from 90 wells in the five study areas. A comparison of predicted and observed VOC presence in the two-county area is then presented.

**STATISTICAL MODELS**

The statistical models presented in this study were developed to describe relations between the quality of shallow ground water and variables representing human activities and local hydrogeologic conditions. The following discussion briefly summarizes the development, application, and testing procedures. Detailed discussion of the statistical techniques are given in Walker and Duncan (1967), Harrell and others (1980), Harrell and Lee (1985), Freeman (1987), Hosmer and Lemeshow (1989), and Helsel and Hirsch (1992).

**Results of Logistic Regressions**

The basis for the development of models presented herein is the network of 90 shallow observation wells within the five areas of differing land use (fig. 1). Randomly distributed well locations within these areas are expected to provide representative data on water quality in the water-table aquifer (LeaMond and others, 1992). All wells were screened within 45 ft of the water table.

Maximum-likelihood logistic regression was used to explore relations between chemical concentrations of ground water and variables representing human activities and local hydrogeologic conditions because it provides a means of relating a mixture of continuous explanatory variables to a binary response variable (the presence or absence of a particular constituent at a specified concentration) (Harrell and Lee, 1985). Explanatory variables used in these models are continuously distributed indicators of the degree and type of human activities at land surface and local hydrogeologic conditions and include several land-use categories, population density, and thickness of the unsaturated zone. Water-quality properties, such as specific conductance, also provide useful explanatory variables. The values of all variables were determined for a 1/2- mi radial area around each of the 90 wells by means of a geographic information system (GIS). A 1/2-mi radius was chosen because this radius represents the distance that water in the water-table aquifer would move in 7 years at an average horizontal flow rate of 1 ft/d; thus, 1987-88 water-quality data collected at each of the 90 wells should reflect the effects of land-use practices from the early and middle 1980’s. Land-use data used to develop the models presented herein represent 1981 patterns; population density represents 1985 conditions. The area within the 1/2-mile radius of each well is assumed to include the predominant sources of contamination near each well (Eckhardt and others, 1989a).

Maximum-likelihood estimates computed by the Newton-Raphson iterative method were used to define the best linear fit between a response variable (presence or absence of a constituent at a specified concentration) and explanatory variables. The maximum-likelihood procedure optimizes the likelihood that the observed water-quality data would be produced from a given set of explanatory-variable slopes (Helsel and Hirsch, 1992). The resulting regression parameters (intercept and slope coefficients) differ significantly from zero at a 95-percent
Figure 1. Location of the five study areas, Long Island, New York.
Table 1. Logistic regression models and measures of goodness of fit for five constituents

[Measures for goodness of fit: G, chi-square statistic of overall model; C, fraction of concordant pairs of predicted probabilities and responses]

<table>
<thead>
<tr>
<th>Constituents</th>
<th>Model equations</th>
<th>G</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Volatile organic compounds (at a concentration of 1 ( \mu g/L ) or greater)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. VOC</td>
<td>( -2.78 + 0.045(\text{HIMEDRES}) + 0.06(\text{COMLU}) )</td>
<td>39</td>
<td>0.87</td>
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<tr>
<td>2. VOC</td>
<td>( -2.80 + 0.31(\text{POPDEN}) + 0.032(\text{MEDRES}) )</td>
<td>39</td>
<td>0.86</td>
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<tr>
<td><strong>Boron (at a concentration of 50 ( \mu g/L ) or greater)</strong></td>
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<td></td>
<td></td>
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<tr>
<td>3. BORON</td>
<td>( -3.96 + 0.0064(\text{CONDUCT}) + 0.37(\text{POPDEN}) + 0.04(\text{AGLU}) )</td>
<td>51</td>
<td>0.90</td>
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<tr>
<td>4. BORON</td>
<td>( -3.06 + 0.052(\text{HIMEDRES}) + 0.053(\text{AGLU}) + 0.12(\text{COMLU}) )</td>
<td>42</td>
<td>0.86</td>
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<tr>
<td><strong>Nitrate (at a concentration of 3 ( mg/L ) as N or greater)</strong></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>5. NITRATE</td>
<td>( -2.10 + 0.35(\text{POPDEN}) + 0.058(\text{AGLU}) + 0.055(\text{MEDRES}) )</td>
<td>37</td>
<td>0.86</td>
</tr>
<tr>
<td>6. NITRATE</td>
<td>( -0.68 + 0.39(\text{POPDEN}) + 0.061(\text{AGLU}) + 0.062(\text{MEDRES}) - 0.032(\text{UNSAT}) )</td>
<td>44</td>
<td>0.88</td>
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<tr>
<td><strong>Insecticides (at a concentration of 0.01 ( \mu g/L ) or greater)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7. CARBAMATE</td>
<td>( -4.09 + 0.0067(\text{AGLU}) )</td>
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<td>0.97</td>
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<tr>
<td>8. ORGANOCHLORINE</td>
<td>( -2.24 + 0.087(\text{AGLU}) + 0.072(\text{HIMEDRES}) - 0.028(\text{UNSAT}) )</td>
<td>52</td>
<td>0.89</td>
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</tbody>
</table>

1. Variable names and descriptions
- POPDEN, Mean area-weighted population density per acre within 1/2-mile radius of well.
  (Source: 1985 Census Bureau block group data)
- HIMEDRES, Percentage of area within 1/2-mile radius of well classified as high-density or medium-density residential, 1 or more dwelling units per acre. (Source: Long Island Regional Planning Board [1982])
- MEDRES, Percentage of area within 1/2-mile radius of well classified as medium-density residential, 1 to 5 dwelling units per acre. (Source: Long Island Regional Planning Board [1982])
- COMLU, Percentage of area within 1/2-mile radius of well classified as commercial. (Source: Long Island Regional Planning Board [1982])
- AGLU, Percentage of area within 1/2-mile radius of well classified as agricultural. (Source: Long Island Regional Planning Board [1982])
- UNSAT, Thickness of unsaturated-zone at well, in feet
- CONDUCT, Specific conductance of well water, (field measured) in microsiemens per centimeter at 25 °C.

Confidence level (\( \alpha = 0.05 \)). Two measures of goodness of fit were used to assess the predictive ability of the logistic regression equations: (1) \( G \), the chi-square statistic for the log-likelihood ratio, which tests the joint effect of explanatory variables in the model, and (2) \( C \), the fraction of concordant predicted and observed values plus one-half the fraction of tied pairs, which is a nonparametric parameter. These measures of goodness of fit were maximized through iterative stepwise procedures (Harrell and others, 1980) by forward selection and backward elimination of explanatory variables. Table 1 presents several models for VOC's.
boron, nitrate, and carbamate and organochlorine pesticide presence and indications of their goodness of fit. Potential sources of these contaminants, and variables found useful in describing their source terms, are identified in the following discussion.

Volatile Organic Compounds

Equations 1 and 2 (table 1) relate the presence of VOC's at concentrations of at least 1 μg/L to variables that reflect sources of VOC contamination. VOC's were detected almost entirely in ground-water samples from the three suburban areas (LeaMond and others, 1992), which are characterized by industrial, commercial, and residential activities. Residue from road surfaces, and leaks and spills of industrial and commercial solvents, such as from dry cleaners and gas stations, can contaminate runoff and recharge before it infiltrates to the ground-water system. VOC's are also components of industrial and household products such as degreasers, furniture strippers, and paint thinners, and thus can be introduced to the ground-water system through cesspools, septic tanks, and leaking sewer lines. Explanatory variables found to be useful in describing VOC source terms include population density, commercial land use, and high- and medium-density residential land use (table 1).

Boron

Equations 3 and 4 (table 1) relate the presence of boron at concentrations of at least 50 μg/L to variables that reflect boron sources. Dissolved-boron concentrations were significantly elevated in agricultural and suburban areas (LeaMond and others, 1992). Primary sources of dissolved boron in Long Island's ground-water system include (1) fertilizers used on commercial crops, and (2) effluent from cesspools, septic tanks, and leaking sewer lines. Boron salts are components of certain fertilizer products, and boron is a component of laundry soaps and detergents. Explanatory variables found to be useful in describing boron-source terms include population density, commercial land use, and high- and medium-density residential land use (table 1).

Nitrate

Equations 5 and 6 (table 1) relate the presence of nitrate at concentrations of at least 3 mg/L to variables that reflect sources of nitrate. Concentrations of nitrate were significantly elevated within the agricultural and suburban areas (LeaMond and others, 1992). Primary sources of nitrate within these areas include (1) fertilizers used on commercial crops, lawns, gardens, and commercial recreational facilities such as golf courses, (2) leakage of effluent from cesspools, septic tanks, and sewer systems and (3) animal feces. Of the 90 wells in the five study areas, 83 indicated nitrate concentrations of at least 0.01 mg/L, the analytical detection limit. For logistic-regression analyses, the response-variable limit was set at 3 mg/L to delineate wells where ground water was most clearly affected by human activities; at 62 of the 90 wells, nitrate concentrations were 3 mg/L or greater. Explanatory variables found to be useful in describing nitrate-source terms include agricultural and residential land use, population density, and thickness of the unsaturated zone (table 1).

Insecticides

Equations 7 and 8 (table 1) relate the presence of carbamate and organochlorine insecticide residues at concentrations of at least 1.0 and 0.01 μg/L respectively, to variables that reflect sources of insecticide. Carbamate insecticides were detected almost entirely in samples from the agricultural area, where they have been applied primarily to control the Colorado potato beetle and golden nematode (Soren and Stelz, 1985); none were detected in samples from the sewered suburban areas (LeaMond and others, 1992). Organochlorine insecticides, the most frequently detected pesticide class in all five study areas, have been applied in agricultural areas to control crop pests and in residential areas to control termites and other insects. Explanatory variables found to be useful in describing carbamate- and organochlorine-source terms include agricultural and high- and medium-density residential land use, and thickness of the unsaturated zone (table 1).

Application of the Statistical Models

Once developed, the linear logistic-regression models can be transformed to predict probabilities of contaminant presence through the logistic function

\[ P(X) = \frac{\exp(\beta_0 + \beta_1 X)}{1 + \exp(\beta_0 + \beta_1 X)} \]

where \( P(X) \) is the probability of contaminant presence.
given the vector $X$ of explanatory variables and the vector $\beta$ of slope parameters and the scalar model intercept, $\beta_0$.

Equation 1 (table 1) was selected to illustrate model application and testing procedures. To predict the probability of VOC presence in the shallow ground-water system of Nassau and Suffolk Counties, the appropriate explanatory variables were quantified for each 1/4-mi$^2$ cell from a gridded overlay of the area. The probabilities computed for each cell through the logistic function were then displayed graphically to illustrate the spatial relation between the explanatory variables and the predicted presence of VOC’s. The probability map of VOC presence at concentrations of at least 1 $\mu$g/L within the two-county area is shown in figure 2.

An independent set of VOC analyses from 378 wells throughout Nassau and Suffolk Counties was spatially compared with the VOC distribution predicted by the model. This data set excluded the 90 wells used for model development. The wells were screened within 45 ft of the water table and were sampled for VOC’s during 1984-90. Each well was assigned either a 1 or 0, depending on VOC detection at a concentration of at least 1 $\mu$g/L, and the cumulative probability distribution of the observed binary presence was then compared with the distribution of predicted probability of presence.

A cumulative-distribution plot showing cumulative probability distributions of observed and predicted probabilities of VOC presence for the two sets of data (the 90 wells from which the predictive equations were developed, and the 378 wells used for comparison) is shown in figure 3. The predicted probabilities closely fit the observed VOC-presence probabilities for the five study areas because the predictive equations were fitted to these data by logistic regression. At probabilities greater than about 0.75, however, the fitted model underpredicts VOC presence observed at the 90-well sites by as much as 8 percent. The close match between predicted probabilities of VOC presence within the two-county area and that for the five study areas indicates that the five land-use areas accurately represent the full range of land uses within the entire two-county area. The second data set was also used to compare predictions of VOC presence, as derived through model 1 (table 1), with the observed presence of VOC’s in the entire two-county area (fig. 2). The resulting underprediction of VOC presence by as much as 30 percent in the low-probability regions indicates that VOC’s are more prevalent in areas with relatively small amounts of commercial and high- and medium-density residential land than indicated by patterns observed in the five land-use areas. The underprediction can also result, in part, from the spatial overlap of some wells, which produces a redundancy of water-quality data.

**SUMMARY AND CONCLUSIONS**

Water-quality data for 90 shallow observation wells in five areas of differing land use on Long Island provided the information necessary to evaluate relations among shallow ground-water quality and variables representing human activities and local hydrogeologic conditions. Maximum-likelihood logistic-regression equations were developed to characterize the probability of VOC, boron, nitrate, and pesticide presence in shallow ground water through explanatory variables such as (1) population density within a 1/2-mi radius of each well, (2) amount of specified types of land use with a 1/2-mi radius of each well, and (3) the thickness of the unsaturated zone at each well site. The explanatory variables were related to the binary response variable (presence or absence of a contaminant at a specified concentration) through logistic regression.

A logistic-regression equation with statistically significant intercept and slope coefficients was selected to predict the probability of VOC presence at concentrations of 1 $\mu$g/L or greater within the shallow ground-water system of Nassau and Suffolk Counties. Model predictions were compared with an independent set of VOC data from 378 shallow wells throughout the two-county area. The underprediction of VOC presence in the two-county area by as much as 30 percent in low-probability regions indicates that, in areas that have relatively small amounts of commercial and high-density and medium-density residential land, VOC’s are more prevalent than indicated by patterns observed within the five specified land-use areas.
\[ \text{VOC} = -2.78 + 0.045 \text{(HIMEDRES)} + 0.06 \text{(COMLU)} \]

**EXPLANATION**

Probability of volatile organic compound detection at concentrations greater than 1.0 microgram per liter

- [ ] <0.25
- [ ] 0.25-0.50
- [ ] 0.50-0.75
- [ ] >0.75

**Figure 2.** Predicted probabilities of volatile organic compound presence at concentrations of 1 microgram per liter or greater.
1.0
0.9
0.8
LU
LU
LU
LU
LU
LU
0.7
0.6
CD
cr
0.5
0.4
0.3

Probability of VOC Presence
In Five Study Areas:
+ - Observed (n = 90)
- - Predicted
In Two-County Area:
* - Observed (n = 378)
* - Predicted

Figure 3. Cumulative probability distributions of observed and predicted probability of volatile organic compound presence at concentrations of 1 microgram per liter or greater.

REFERENCES


Evaluating the Effect of Land Use and Sampling Depth on Ground-Water Quality, Long Island, New York

By Paul E. Stackelberg

Abstract

The effect of nonpoint-source contamination was statistically evaluated through a comparison of water-quality data collected from two depth intervals at 153 wells in five areas of differing land use on Long Island. Each area was delineated to represent a predominant land use; the areas were categorized as (1) suburban with long-term sewering, (2) suburban with recent sewering, (3) suburban without sewers, (4) agricultural, and (5) undeveloped. The depth zones were delineated on the basis of estimated traveltime of ground water along vertical flow paths from the water table to each well screen's midpoint. Wells were classified as shallow (estimated traveltimes of less than 10 years) or intermediate (estimated traveltimes between 10 and 100 years).

Concentrations of several inorganic constituents and values of field properties were found to differ significantly among land-use areas and depth zones. Median constituent concentrations tend to be (1) highest, and the concentration ranges the widest, in samples from the agricultural area, (2) lowest, and the concentration ranges the smallest, in samples from the undeveloped area, and (3) intermediate to high in samples from the suburban areas. Volatile organic compounds (VOC's) were detected only in the suburban areas. A common source of nonpoint-source contamination in agricultural and residential areas is fertilizers used on commercial crops, lawns, gardens, and golf courses. Other sources of inorganic contaminants and VOC's in residential areas include (1) effluent from cesspools, septic tanks, and leaking sewers, (2) road-deicing salts, and (3) runoff contaminated by road residues and by chemicals commonly used at industrial and commercial facilities. A decrease in concentrations of most inorganic constituents with depth is attributed to (1) physical and chemical reactions that remove constituents from solution, and (2) dilution by advection and hydrodynamic dispersion along flow paths.

INTRODUCTION

Relations between land use and ground-water quality in Nassau and Suffolk Counties have been investigated as part of the U.S. Geological Survey's Toxic Substances Hydrology Program since the early 1980's (Eckhardt and others, 1988, and LeaMond and others, 1992). The most recent phase of the study was begun in 1990 and was designed to evaluate statistically the effects of land use and depth on ground-water quality beneath five areas of differing land use. The five areas were delineated according to predominant land use and duration of sewering in 1984 and are categorized as (1) suburban with long-term sewering (longer than 22 years), (2) suburban with recent sewering (less than 8 years), (3) suburban without sewers, (4) agricultural, and (5) undeveloped (fig. 1). All five areas lie along the regional ground-water divide, where vertical ground-water flow components cause contaminants introduced at or near land surface to be transported deeper into the aquifer system than elsewhere. Water-quality data from 207 randomly selected wells screened in shallow, intermediate, and deep zones beneath the five study...
Figure 1. Location of the five study areas on Long Island, New York.
areas were statistically evaluated to determine (1) differences in water quality among the five areas and shallow and intermediate depth zones, (2) differences in water quality among the suburban areas and all three depth zones, and (3) whether sewerage within the suburban areas has resulted in an improvement in ground-water quality. Depth zones were delineated on the basis of estimated traveltime of ground water along vertical flow paths from the water table to each well screen’s midpoint. Wells were classified as shallow (estimated traveltimes of less than 10 years), intermediate (estimated traveltimes from 10 to 100 years), and deep (estimated traveltime longer than 100 years).

This paper summarizes (1) the data-collection and statistical methods, and (2) the effects of land use and depth on water quality in the shallow and intermediate-depth zones of the five study areas.

**STUDY METHODS**

The approach used in this study was based on the premise that contamination of ground water by human activities can be considered a function of land use—that is, land uses determine the amounts and types of chemicals that are applied to the land surface and, thus, the amounts and types of contaminants that reach ground water (Helsel and Ragone, 1984). The study entailed three procedures: (1) collection of water-quality data from a network of 153 wells, (2) classification of wells as shallow or intermediate on the basis of estimated ground-water residence time, and (3) statistical analyses of water-quality data.

**Data Collection**

Water samples were collected from June 1987 through September 1988 from a network of 153 wells within the five study areas. In all, 83 shallow wells and 70 intermediate-depth wells were sampled. The shallow zone was represented by 11 to 20 wells in each study area, and the intermediate zone by 10 to 17 wells in each study area.

Wells were classified as monitoring, public supply, or unspecified withdrawal. At each monitoring well, water levels were measured before pumping, at least three casing volumes were evacuated, and drawdown, specific conductance, pH, and temperature were allowed to stabilize before sampling. At each public-supply and unspecified-withdrawal well, at least three casing volumes of water were evacuated, and measurements of specific conductance, pH, and temperature were made before sampling.

The water-quality data analyzed herein, and additional details of well-locating procedures and sampling methods, are given in Stackelberg (unpublished data on file in Syosset, N.Y. office of U.S. Geological Survey) and LeaMond and others (1992).

**Well-Depth Classification**

Classification of wells as shallow or intermediate was based on the traveltime of ground water along vertical flow paths from the water table to the midpoint of each well screen to ensure that all wells within a given depth zone would provide samples of similar age. Vertical flow rates were calculated from cell-to-cell flow rates by the regional ground-water-flow model of Long Island (H.T. Buxton and D.A. Smolensky, U.S. Geological Survey, written commun., 1990), which simulates ground-water flow under steady-state conditions of 1968-75. These years represent a period in which precipitation rates paralleled long-term average rates, and ground-water pumpage was uniform (S.M. Feldman, U.S. Geological Survey, oral commun., 1990). The vertical flow rates were then used to calculate traveltimes along vertical flow paths from the water table to each screen's midpoint. Although this method does not address traveltimes through the unsaturated zone, the mean unsaturated-zone thickness is similar in all five land-use areas, except in the suburban unsewered area, where Tukey’s test indicates it to be significantly greater than in the agricultural or undeveloped areas. (An explanation of Tukey’s test is provided in the following section.) Shallow wells were those estimated to tap water with a residence time of less than 10 years, and intermediate wells were those estimated to obtain water 10 to 100 years old.

**Statistical Analyses**

Nonparametric statistical procedures and contingency-table analyses were used to evaluate the effect of land use and sampling depth on constituent concentrations. Nonparametric procedures, such as analysis of variance (ANOVA) on rank-transformed data, are robust—that is, they are insensitive to outlying values and assumptions of equal variance or
normality (Helsel and Hirsch, 1992; Iman and Conover, 1983). Contingency-table analyses provide a means of evaluating highly censored data sets. (Censored data sets contain values whose concentration is reported as “less than the analytical detection limit.”) These statistical procedures are used to assess whether water-quality data differ significantly among land-use and depth categories. Two-way factorial ANOVA’s on rank-transformed water-quality data were used to examine the effect of land use and depth simultaneously. The null hypothesis for this test states that mean concentration ranks are identical among all land-use and depth groups; thus no effects are due to land use, depth, or their interaction. If interaction is found to be significant, the effect of depth on mean concentration ranks differs among land-use areas. Without significant interaction, the effect of depth on mean concentration ranks is identical among all land-use areas (Helsel and Hirsch, 1992). If the null hypothesis was rejected by the ANOVA test, indicating that at least one mean concentration-rank value differed from another, Tukey’s honest significant difference test (Tukey’s test) was performed to determine which means differed.

Contingency-table analyses were used to examine differences in water quality among the five study areas and two depth zones for constituents whose censored values constituted more than 50 percent of the total values. Contingency-table analyses do not evaluate the effects of multiple factors simultaneously; therefore, separate tests were performed on land-use and sampling-depth data to evaluate their effects on constituent-detection rates. The null hypotheses tested were that the proportion of samples with constituent detections was the same for each study area or depth zone; rejection of the null hypothesis indicates that the proportion of samples with constituent detections differed among land-use areas or depth zones. If a contingency-table analysis indicated that the proportion of samples in which a constituent was detected differed among study areas or depth zones, individual-cell chi-square statistics were examined to determine which areas or depth zones had more or less than the expected proportion of constituent detections. The positive or negative sign of the difference between observed and expected frequencies indicates more (+), or fewer (-), detections within that area or depth zone, and the magnitude of the chi-square statistic indicates cells contributing most to the rejection of the null hypothesis (Helsel and Hirsch, 1992).

The level of significance (alpha) for all hypothesis testing reported herein is 0.05. Results from ANOVA and contingency table test are reported as p-values that indicate the strength of the evidence to accept or reject the null hypothesis. The null hypothesis is rejected for all p-values reported as less than 0.05; the smaller the p-value, the stronger the evidence for rejection.

Water-quality data for selected constituents are represented as box plots, which indicate the median, the data variation and skewness, and the absence or presence of unusual “outside” or “far-outside” values (Helsel and Hirsh, 1992). Summary statistics for water-quality data that contained censored values were calculated through a log-probability regression technique (Helsel and Hirsh, 1992), a robust procedure that minimizes rates of root mean square error. Results from Tukey’s test are presented as letters above the box plots for each land-use area. Groups of data with at least one of the same letters do not differ significantly from one another.

**EFFECTS OF LAND USE AND SAMPLING DEPTH ON GROUND-WATER QUALITY**

The effect that land use, sampling depth, and interaction between land use and depth have on constituent concentrations are reported as p-values in tables 1 and 2. Summary statistics for samples from the shallow and intermediate zone of each area are reported in table 3, which includes results of Tukey’s test to indicate whether the mean concentration ranks from the combination of shallow and intermediate-depth samples in each area are similar among study areas. Results from a contingency-table analysis for sulfate are given in table 4. Median concentrations from the combination of shallow- and intermediate-depth samples of a particular area are reported in the text.

Concentrations of inorganic constituents and field-measured properties, except pH, differed significantly among study areas and, except for dissolved oxygen, differed significantly between depth zones (tables 1 and 2). Interaction was found to be significant for temperature and concentrations of nitrate, potassium, and magnesium (table 1).
Table 1. p-values from two-way factorial ANOVA’s indicating the effect of land use, sampling depth, and their interaction on field-measured properties and inorganic-constituent concentrations from both depth zones of the five study areas, Long Island, New York

<table>
<thead>
<tr>
<th>Properties and constituents</th>
<th>Land use</th>
<th>Depth zone</th>
<th>Interaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific conductance</td>
<td>0.0001</td>
<td>0.0001</td>
<td>0.1090</td>
</tr>
<tr>
<td>pH</td>
<td>0.5155</td>
<td>0.0270</td>
<td>0.1121</td>
</tr>
<tr>
<td>Dissolved oxygen</td>
<td>0.0001</td>
<td>0.2541</td>
<td>0.1950</td>
</tr>
<tr>
<td>Temperature</td>
<td>0.0001</td>
<td>0.0001</td>
<td>0.0031</td>
</tr>
<tr>
<td>Nitrate</td>
<td>0.0001</td>
<td>0.0001</td>
<td>0.0361</td>
</tr>
<tr>
<td>Potassium</td>
<td>0.0001</td>
<td>0.0001</td>
<td>0.0071</td>
</tr>
<tr>
<td>Sodium</td>
<td>0.0001</td>
<td>0.0001</td>
<td>0.8183</td>
</tr>
<tr>
<td>Chloride</td>
<td>0.0002</td>
<td>0.0001</td>
<td>0.4011</td>
</tr>
<tr>
<td>Calcium</td>
<td>0.0001</td>
<td>0.0001</td>
<td>0.0541</td>
</tr>
<tr>
<td>Magnesium</td>
<td>0.0001</td>
<td>0.0121</td>
<td>0.0205</td>
</tr>
</tbody>
</table>

Table 2. p-values from contingency-table analyses indicating the effect of land use and sampling depth on the proportion of samples from both depth zones with sulfate and volatile organic compound detections [<, less than]

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Land use</th>
<th>Sampling Depth</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfate (all five study areas)</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Volatile organic compounds (suburban areas only):</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,1,1-trichloroethane</td>
<td>0.069</td>
<td>0.135</td>
</tr>
<tr>
<td>Trichloroethene</td>
<td>0.144</td>
<td>0.660</td>
</tr>
<tr>
<td>Tetrachloroethene</td>
<td>0.052</td>
<td>0.758</td>
</tr>
</tbody>
</table>

The highest median values for specific conductance (325 μS/cm) and concentrations of nitrate (7.48 mg/L as N), potassium (3.9 mg/L), calcium (27.9 mg/L), and magnesium (7.1 mg/L) resulted from the combination of shallow and intermediate depth zones in the agricultural area, but Tukey’s test results indicates that the mean concentration ranks for these constituents in the agricultural area do not differ significantly from those for one or more of the suburban areas, except for potassium, whose mean rank in the agricultural area is significantly higher than that from any other area (table 3). Elevated concentrations of these constituents in the agricultural and suburban areas result primarily from (1) fertilizers used on crops, lawns, and golf courses, and (2) leakage from cesspools, septic tanks, and sewer systems. Road-deicing salts will also elevate specific conductance, especially in suburban areas, where road networks are extensive.

Results from contingency-table analysis indicate that sulfate detection in samples from both depth zones differed significantly among study areas (table 2). The sign of the difference between observed and expected frequencies and the magnitude of each cell’s chi-square statistic (table 4) indicates that the two depth zones in the long-term sewered and agricultural areas together have more sulfate detections, and the unsewered area had fewer, than would be expected if all land-use areas were alike; therefore, sulfate appears to be more prevalent in the long-term sewered suburban and agricultural areas than elsewhere (table 4). The proportion of samples from both depth zones in each study area with sulfate detections ranged from 91 percent in the agricultural area to 46 percent in the unsewered suburban area. Although sulfate was detected frequently in samples from both depth zones of the undeveloped area (79 percent), concentrations in this area were lower than elsewhere. Elevated concentrations of sulfate in the agricultural area probably result from fertilizers; the highest sulfate concentration (920 mg/L) in all five areas was in the intermediate zone of the agricultural area. Sulfate concentrations were also elevated in the suburban areas, probably as a result of lawn and garden fertilizers and effluent from cesspools, septic tanks, and leaking sewer lines.
Table 3. Summary statistics for samples from the shallow and intermediate zones of each study area, Long Island, New York

[Numbers in parentheses represent the number of wells sampled; IQR, interquartile range; Tukey’s test, results of Tukey’s Studentized test]

<table>
<thead>
<tr>
<th>Study Areas (S, shallow wells; I, intermediate wells)</th>
<th>Long-term sewered</th>
<th>Recently sewered</th>
<th>Unsewered</th>
<th>Agricultural</th>
<th>Undeveloped</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Properties, constituents, and statistics</strong>¹</td>
<td>S I</td>
<td>S I</td>
<td>S I</td>
<td>S I</td>
<td>S I</td>
</tr>
<tr>
<td><strong>Field-measured Properties</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Specific conductance (microsiemens per centimeter)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Median</td>
<td>280</td>
<td>189</td>
<td>299</td>
<td>139</td>
<td>222</td>
</tr>
<tr>
<td>IQR</td>
<td>105</td>
<td>158</td>
<td>173</td>
<td>191</td>
<td>196</td>
</tr>
<tr>
<td>Tukey’s test</td>
<td>A</td>
<td>AB</td>
<td>BC</td>
<td>A</td>
<td>C</td>
</tr>
<tr>
<td><strong>pH</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Median</td>
<td>5.65</td>
<td>5.65</td>
<td>5.50</td>
<td>5.80</td>
<td>5.60</td>
</tr>
<tr>
<td>IQR</td>
<td>0.50</td>
<td>0.65</td>
<td>0.55</td>
<td>0.90</td>
<td>0.80</td>
</tr>
<tr>
<td>Tukey’s test</td>
<td>A</td>
<td>A</td>
<td>A</td>
<td>A</td>
<td>A</td>
</tr>
<tr>
<td><strong>Dissolved oxygen (milligrams per liter)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Median</td>
<td>6.9</td>
<td>3.3</td>
<td>5.8</td>
<td>6.0</td>
<td>8.0</td>
</tr>
<tr>
<td>IQR</td>
<td>6.1</td>
<td>3.6</td>
<td>4.3</td>
<td>4.3</td>
<td>3.4</td>
</tr>
<tr>
<td>Tukey’s test</td>
<td>A</td>
<td>A</td>
<td>A</td>
<td>B</td>
<td>B</td>
</tr>
<tr>
<td><strong>Temperature (degrees Celsius)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Median</td>
<td>14.3</td>
<td>14.4</td>
<td>14.4</td>
<td>12.6</td>
<td>13.0</td>
</tr>
<tr>
<td>IQR</td>
<td>0.9</td>
<td>3.5</td>
<td>1.1</td>
<td>1.8</td>
<td>1.6</td>
</tr>
<tr>
<td>Tukey’s test</td>
<td>A</td>
<td>A</td>
<td>A</td>
<td>B</td>
<td>BC</td>
</tr>
<tr>
<td><strong>Constituents (in milligrams per liter)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Nitrate</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Median</td>
<td>5.12</td>
<td>2.18</td>
<td>5.74</td>
<td>4.47</td>
<td>6.91</td>
</tr>
<tr>
<td>IQR</td>
<td>2.19</td>
<td>4.63</td>
<td>6.86</td>
<td>5.30</td>
<td>9.88</td>
</tr>
<tr>
<td>Tukey’s test</td>
<td>A</td>
<td>A</td>
<td>A</td>
<td>A</td>
<td>A</td>
</tr>
<tr>
<td><strong>Potassium</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Median</td>
<td>2.7</td>
<td>2.1</td>
<td>3.9</td>
<td>0.7</td>
<td>1.9</td>
</tr>
<tr>
<td>IQR</td>
<td>2.2</td>
<td>1.1</td>
<td>2.9</td>
<td>0.7</td>
<td>2.3</td>
</tr>
<tr>
<td>Tukey’s test</td>
<td>B</td>
<td>B</td>
<td>BC</td>
<td>A</td>
<td>C</td>
</tr>
<tr>
<td><strong>Sodium</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Median</td>
<td>17.5</td>
<td>14.5</td>
<td>23.0</td>
<td>11.0</td>
<td>17.5</td>
</tr>
<tr>
<td>IQR</td>
<td>14.5</td>
<td>16.7</td>
<td>22.0</td>
<td>12.0</td>
<td>15.0</td>
</tr>
<tr>
<td>Tukey’s test</td>
<td>A</td>
<td>A</td>
<td>AB</td>
<td>BC</td>
<td>C</td>
</tr>
<tr>
<td><strong>Chloride</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Median</td>
<td>32.0</td>
<td>28.2</td>
<td>30.8</td>
<td>13.7</td>
<td>22.0</td>
</tr>
<tr>
<td>IQR</td>
<td>24.8</td>
<td>27.3</td>
<td>36.2</td>
<td>12.9</td>
<td>22.1</td>
</tr>
<tr>
<td>Tukey’s test</td>
<td>A</td>
<td>AB</td>
<td>BC</td>
<td>AB</td>
<td>C</td>
</tr>
<tr>
<td><strong>Calcium</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Median</td>
<td>21.7</td>
<td>9.3</td>
<td>16.8</td>
<td>6.9</td>
<td>12.5</td>
</tr>
<tr>
<td>IQR</td>
<td>10.4</td>
<td>11.1</td>
<td>9.2</td>
<td>12.9</td>
<td>13.9</td>
</tr>
<tr>
<td>Tukey’s test</td>
<td>AB</td>
<td>B</td>
<td>C</td>
<td>BC</td>
<td>A</td>
</tr>
<tr>
<td><strong>Magnesium</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Median</td>
<td>3.9</td>
<td>2.9</td>
<td>2.8</td>
<td>2.6</td>
<td>4.5</td>
</tr>
<tr>
<td>IQR</td>
<td>3.3</td>
<td>1.8</td>
<td>0.9</td>
<td>4.0</td>
<td>3.0</td>
</tr>
<tr>
<td>Tukey’s test</td>
<td>AB</td>
<td>BC</td>
<td>BC</td>
<td>BC</td>
<td>A</td>
</tr>
</tbody>
</table>

¹ Tukey’s test results are presented as letters. Groups of data with at least one of the same letters do not differ significantly from one another.
Table 4. Contingency-table analysis showing individual-cell frequency, expected frequency, and chi-square statistics for sulfate detection in samples from both depth zones of the five study areas on Long Island, New York.

<table>
<thead>
<tr>
<th>Study area</th>
<th>Detected</th>
<th>Not detected</th>
</tr>
</thead>
<tbody>
<tr>
<td>Long-term sewered</td>
<td></td>
<td></td>
</tr>
<tr>
<td>frequency</td>
<td>29</td>
<td>4</td>
</tr>
<tr>
<td>expected frequency</td>
<td>24.16</td>
<td>8.84</td>
</tr>
<tr>
<td>chi-square</td>
<td>0.97</td>
<td>2.65</td>
</tr>
<tr>
<td>Recently sewered</td>
<td></td>
<td></td>
</tr>
<tr>
<td>frequency</td>
<td>27</td>
<td>10</td>
</tr>
<tr>
<td>expected frequency</td>
<td>27.08</td>
<td>9.91</td>
</tr>
<tr>
<td>chi-square</td>
<td>&lt;.00</td>
<td>&lt;.00</td>
</tr>
<tr>
<td>Unsewered</td>
<td></td>
<td></td>
</tr>
<tr>
<td>frequency</td>
<td>17</td>
<td>20</td>
</tr>
<tr>
<td>expected frequency</td>
<td>27.08</td>
<td>9.91</td>
</tr>
<tr>
<td>chi-square</td>
<td>0.94</td>
<td>10.26</td>
</tr>
<tr>
<td>Agricultural</td>
<td></td>
<td></td>
</tr>
<tr>
<td>frequency</td>
<td>20</td>
<td>2</td>
</tr>
<tr>
<td>expected frequency</td>
<td>16.10</td>
<td>5.89</td>
</tr>
<tr>
<td>chi-square</td>
<td>0.94</td>
<td>2.57</td>
</tr>
<tr>
<td>Undeveloped</td>
<td></td>
<td></td>
</tr>
<tr>
<td>frequency</td>
<td>19</td>
<td>5</td>
</tr>
<tr>
<td>expected frequency</td>
<td>17.57</td>
<td>6.43</td>
</tr>
<tr>
<td>chi-square</td>
<td>0.12</td>
<td>0.32</td>
</tr>
</tbody>
</table>

The highest median temperature (14.4°C), and the highest median concentration of sodium (17 mg/L) and chloride (31.2 mg/L) resulted from the combination of samples from shallow and intermediate depths from the long-term sewered area, but results of Tukey’s test indicate that mean concentration ranks for these constituents in the long-term sewered area do not differ significantly from those for at least one other suburban area and that the mean concentration rank for chloride in the long-term sewered area does not differ significantly from that in the agricultural area (table 3). Elevated temperatures in the suburban areas are probably due to the absorption of heat from artificial surfaces such as asphalt or concrete before the infiltration of recharge. Also, water that stands in recharge basins before infiltrating could absorb solar energy and thereby increase in temperature. The elevated sodium and chloride concentrations in suburban areas is attributed to the application of deicing salts on the extensive road networks. These constituents are also found in some household cleaning products and are a component of cesspool, septic-tank, and sewerline effluents.

The highest median concentration for dissolved oxygen (10.55 mg/L) resulted from the combination of shallow and intermediate samples in the undeveloped area; however, Tukey’s test results indicate that the mean concentration rank for this area does not differ significantly from those for the agricultural or unsewered suburban areas, and these three areas have significantly higher values than the sewered suburban areas (table 3). Processes that could accelerate the depletion of dissolved oxygen within the sewered suburban areas include nitrification and increased bacterial activity. Nitrogen introduced to the groundwater system in the form of ammonium by cesspools, septic tanks, and sewerlines is converted to nitrogen and nitrate through oxidation, which also consumes dissolved oxygen. Additionally, dissolved organic carbon that is introduced from the same sources in sewered suburban areas could fuel bacterial activity that also consumes dissolved oxygen.

Examination of p-values in tables 1 and 2 indicates that concentrations of each inorganic constituent, and measurements of each field property except dissolved oxygen, differed significantly with depth. The highest median concentration of these constituents and field-measured properties, except pH, were in samples from the shallow zone of all five study areas combined. Decreasing concentrations of these inorganic constituents with depth probably results from (1) physical and chemical reactions that remove these constituents from solution, and (2) dilution through advection and hydrodynamic dispersion as constituents move along flow paths. The highest median pH value was from samples from the intermediate zone of all five study areas combined. The increase in pH with depth is most likely due to the oxidation of organic matter; this is most apparent in the undeveloped area and least apparent in the agricultural and suburban areas (table 3). The smaller increase in pH with depth in the agricultural and suburban areas than in the undeveloped area could be due to the process of nitrification, which, in addition to consuming dissolved oxygen, produces hydrogen ions that lower the pH.

Dissolved-oxygen concentrations were not found to change significantly with depth; thus, concentrations in the intermediate zone of all five...
study areas combined were similar to those in the shallow zone. The extent to which dissolved oxygen concentrations can be maintained with depth depends in part on (1) the hydraulic properties of soils and aquifer materials through which ground water flows, and (2) the rate at which oxygen-depleting processes are occurring within the unsaturated and saturated zones. Elevated dissolved-oxygen concentrations in the intermediate zone indicate that (1) soils and aquifer materials in the five study areas are highly permeable, well drained, and subsequently well aerated, and (2) processes that deplete dissolved oxygen concentrations (such as nitrification, bacterial activity, and oxidation of organic matter), although not completely absent, are insufficient to exhaust dissolved-oxygen supplies within the depths examined.

Interaction between the effects of land use and sampling depth was significant for temperature, nitrate, potassium, and magnesium (table 1); indicating that the effect of depth differs among the land-use areas. This effect is illustrated in table 3 and figure 2, where concentrations of the inorganic constituents are seen to decrease from the shallow to the intermediate zone of each area except the undeveloped area, and temperatures decrease from the shallow to intermediate zone of each area except the long-term sewered suburban area.

The most commonly detected VOC’s were 1,1,1-trichloroethane (TCA), trichloroethylene (TCE), and tetrachloroethylene (PCE), whose maximum concentrations were 12,000, 660, and 280 \( \mu \)g/L, respectively. VOC’s are introduced to the ground water of suburban areas primarily from industrial, commercial, and residential activities. Accidental leaks and spills of industrial chemicals and hydrocarbons from commercial facilities such as dry cleaners and gas stations, and residue from road surfaces, could contaminate runoff before it infiltrates to the ground-water system. VOC’s are also components of industrial and household products such as degreasers, furniture strippers, and paint thinners, and, thus, can be introduced to the ground-water system as effluent from cesspools, septic tanks, and leaking sewer lines. These compounds were detected solely within the three suburban areas; thus, the following paragraph addresses their presence and spatial distribution only within those areas.

Of all samples from the shallow and intermediate zone of the long-term sewered area, 57 percent contained VOC’s, as did 54 percent of those from the recently sewered suburban area, and 27 percent of those from the unsewered suburban area. Contingency-table results indicate that the proportion of samples from both zones that contained these compounds did not differ among suburban areas significantly (table 2), although the evidence to accept the null hypothesis that the proportion of PCE detections were equal among all areas was not strong (p-value = 0.052). Detection frequencies for these compounds did not differ significantly between the two depth zones; therefore, the proportion of samples with VOC detection from the intermediate zone of all suburban areas combined did not differ significantly from the proportion for the shallow zones.

**SUMMARY**

Contamination from nonpoint sources has altered the quality of water in Long Island’s aquifer system. The spatial distribution of the contaminants within the aquifer system can be related to their depth below the water table and to land-use patterns.

The concentrations of several inorganic constituents, and volatile organic compounds (VOC’s), and values for field-measured properties in ground water, differ significantly among the five study areas. Statistical evaluation of constituent concentrations and detection frequencies indicated that median concentrations tend to be (1) highest, and concentration ranges the widest, in the agricultural area, (2) lowest, and the concentration ranges the smallest, in the undeveloped area, and (3) intermediate to high in suburban areas. VOC’s were detected only in samples of ground water from suburban areas. A major source of ground-water contamination within agricultural and residential areas is probably the fertilizers used on commercial crops, lawns, gardens, and commercial recreational facilities such as golf courses. Application of these products results in elevated concentrations of nitrate, and sulfate, and inorganic constituents such as calcium, potassium, and magnesium. An additional source of these constituents, especially in high-density residential areas, is cesspool, septic tank, and leaking-sewerline effluent, which contains human wastes and common household-cleaning products. Road-deicing salts applied on extensive road networks within suburban
Figure 2. Distribution of temperature, nitrate, potassium, and magnesium in water from the shallow and intermediate zones of the five study areas, Long Island, New York.
areas cause elevated concentrations of sodium and chloride. Sources of VOC contamination within suburban areas include (1) residues from the extensive road networks, (2) commercial and industrial facilities commonly associated with residential areas such as dry cleaners and gas stations, and (3) effluent from cesspools, septic tanks, and sewerlines.

The quality of ground water differs significantly with depth; the concentrations of most inorganic constituents and values of field properties decrease from the shallow to the intermediate zone of the aquifer. This decrease is attributed to (1) physical and chemical reactions that remove constituents from solution, and (2) dilution by advection and hydrodynamic dispersion as constituents move along flow paths. Dissolved-oxygen concentrations did not decrease significantly with depth, indicating that (1) aquifer materials within the five study areas are highly permeable, well-drained, and well aerated at depth, and (2) processes that deplete dissolved oxygen are insufficient to exhaust the dissolved oxygen at the depths examined.

REFERENCES


Use of Flowpath Simulation to Determine Contributing Areas and Traveltimes of Nonpoint-Source Ground-Water Contamination, Gloucester County, New Jersey

By Anthony S. Navoy

Abstract

The area of direct surficial recharge, potentially affected by nonpoint-source contamination, to the Potomac-Raritan-Magothy aquifer system in Gloucester County, New Jersey, extends a maximum of 0.5 to 2 miles down dip from the outcrop area as determined by use of a finely discretized ground-water-flow model and flow-path simulation by use of particle-tracking analysis. The areas contributing water to three water-supply wells, determined by simulation, were found to contain chemical-product-manufacturing or petroleum-refining land use. A relatively short minimum travel time of 30 years between the petroleum-refining land use and one of the wells indicates that contamination by volatile organic compounds is likely. The minimum traveltimes of greater than 50 years to the other two wells indicate that, to date, contamination by volatile organic compounds is not likely. These interpretations are consistent with available water-quality data. The results of the analysis also indicate that the two wells heretofore unaffected by contamination probably will be affected by contamination in the future and that the concentrations of volatile organic compounds in water from the affected well are likely to increase. The method of analysis used in this investigation could be applied to other locales provided that a finely discretized ground-water-flow model and high-resolution land-use data are available.

INTRODUCTION

Ground-water contamination can pose a significant threat to potable water supplies. Large areas sometimes can appear to be affected by the same or similar types of contaminants whose sources either are not evident or are too numerous to evaluate individually. The term “nonpoint-source contamination” has been applied to these situations. The ability to mitigate the problems created by contamination, however, is predicated on understanding the origins of the contamination and transport of the contaminants. Evaluation and mitigation of nonpoint-source contamination is difficult as a result of the uncertainties involved in the delineation of sources and transport characteristics.

Previous investigators (Vowinkel and Battaglin, 1989b; Eckhardt and others, 1989) have approached the study of nonpoint-source ground-water contamination with the use of stochastic methods to relate land use within circular buffer zones surrounding wells to the quality of water in the well in order to discern possible sources of the contamination. This approach can be particularly useful to assess large amounts of data and determine the likely extent of contamination. With the stochastic approach, however, local characteristics of the ground-water-flow system cannot be incorporated into the analysis. These characteristics include variations in hydraulic properties, location and intensity of withdrawals, or variations in hydrostratigraphy, and are especially important in determining the origins and transport of observed contamination. The determination of the

1U.S. Geological Survey, West Trenton, N. J.
areas contributing direct surficial recharge to the
ground-water-flow system and the time of travel from
these sources to a well is of particular interest in this
analysis; however, these factors cannot be established
adequately by means of the stochastic methods.

The Potomac-Raritan-Magothy aquifer system
in southern New Jersey is an opportune case-study
area to develop methods for evaluating the origins and
transport of nonpoint-source ground-water
contamination. The aquifer system is the primary
water-supply source for the Camden, New Jersey,
metropolitan area, including parts of Burlington,
Camden, and Gloucester Counties, shown in figure 1.
The Potomac-Raritan-Magothy aquifer system in the
Cretaceous Potomac Group, Raritan Formation, and
Magothy Formation is part of the southeastward-
dipping wedge of Coastal Plain sediments composed
of gravels, sands, silts, and clays of Cretaceous to
Holocene age (Zapecza, 1989), and is locally
differentiated into three components--the upper, middle,
and lower aquifers (figs. 1B and 1C). These aquifers are
separated by intervening leaky confining units.

About 100 million gallons per day of water is
pumped from the aquifer system in this area (Camp
Dresser & McKee, Inc., 1984), regionally creating a
large cone of depression in the aquifer system's
potentiometric surface. Land use in the outcrop area,
contributing recharge to the aquifer system, is diverse
and includes manufacturing, trade, residences, and
agriculture, which have contributed contaminants that
have been observed in regional-scale ground-water
sampling investigations (Fusillo and others, 1984,
tables 4, 5, and 6; Vowinkel and Battaglin, 1989a;
Ervin and others, 1994). The Planning Department of
Gloucester County maintains maps that contain a
detailed accounting of the land use in the outcrop area.
These maps can be used to facilitate an investigation
of nonpoint-source contamination in Gloucester
County at a high resolution with the assumption that
land use can be used as a surrogate for possible
contaminant sources.

This paper summarizes the preliminary findings
of an ongoing study to develop a method for
investigating nonpoint-source ground-water
contamination in areas of complex hydrogeology with
multiple sites of ground-water withdrawal by use of
ground-water-flow simulation -- in particular, the
determination of areas contributing direct recharge
from the land surface and the time of travel from these
sources to a well.

**METHODS**

A ground-water-flow model of the Potomac-
Raritan-Magothy aquifer system in the Camden area
was developed by Navoy and Carleton (in press), by
using the MODFLOW computer code (McDonald and
Harbaugh, 1988), as a tool to evaluate withdrawal-
management strategies. The design of this model is
appropriate to the objectives of this study, as the model
grid is finely discretized in the aquifer system's
outcrop area. The model consists of five aquifer layers
in a quasi-three-dimensional representation of the
hydrogeologic units. The upper, middle, and lower
aquifers are each represented by a model layer. Two
additional layers represent stratigraphically younger
aquifers overlaying the confined aquifer system to
account for vertical flow across the model boundary.
The horizontal boundaries of the model are indicated
in figure 1A. The horizontal flows across the
boundaries of the model from adjacent areas in the
Coastal Plain were derived from the more coarsely
discretized Regional Aquifer-Systems Analysis
(RASA) model of the entire New Jersey Coastal Plain
(Martin, 1990). A no-flow boundary represents the
crystalline rocks underlying the aquifer system.

The simulated aquifers were discretized
horizontally into a variably spaced grid having 99
rows and 106 columns, and oriented approximately
parallel to the Fall Line (fig. 1A) and the strike of the
geologic units. The smallest cells represent an area
880 by 1,650 feet and are in proximity to aquifer
system's outcrop and the Delaware River. The largest
cells represent an area 2,200 by 3,300 feet and are
generally located in the downdip, southeastern part of
the model, away from the outcrop area. The model
was calibrated satisfactorily to historical water-level
data. Detailed information on the design and
validation of the model is available in Navoy and
Carleton (in press).

Ground-water flowpaths were examined to
determine the recharge contributing areas and estimate
taveltimes within the ground-water system. This
analysis was accomplished by using a particle-
tracking technique. The simulated paths of
hypothetical particles as they travel through the
ground-water-flow field are determined as a function
of time (Pollock, 1988). Porosities of 25 percent for
the aquifer layers and 40 percent for confining units
were used. A steady-state flow simulation was
performed with average withdrawals for 1983-88 and
ground-water flowpaths were determined with the
Figure 1. A. Location of study area, B. outcrop areas and location of simulated downdip limit of direct surficial recharge in the Potomac-Raritan-Magothy aquifer system, and C. generalized hydrogeologic section through the study area.
MODPATH particle tracker (Pollock, 1989). The fixed withdrawal rates used for the particle tracking are not entirely realistic, from a regional perspective, because rates were lower in the past. In the vicinity of the outcrop, however, rates have been fairly stable for the past several decades (Camp Dresser & McKee, Inc., 1984). Withdrawals from the aquifer system in the study area are not likely to increase substantially in the future because the New Jersey Department of Environmental Protection and Energy has initiated measures to restrict future increases in withdrawals (New Jersey Department of Environmental Protection, 1986). Thus, these rates are likely to be representative of withdrawals from the aquifer system in the study area for the foreseeable future and extrapolation of the results of the flowpath analysis into the future probably is valid.

Under natural, predevelopment conditions, ground water in the study area discharged to the Delaware River and its tributaries. The aquifer system within the study area became a recharge zone with the advent of water-supply pumpage. Conceptually, a volume of the aquifer system now contains water whose origin is, in part, direct recharge from the land surface at the outcrop in the study area. Recharge also originates from streams, including the Delaware River; however, the recharge from the land surface is the focus of this investigation. The extent of the direct surficial recharge was evaluated with the particle tracker. Hypothetical particles were placed on the top of all model cells within the aquifer-system outcrop area. These particles were tracked forward into the aquifer. The part of the aquifer in which the particles traveled within a travel time of 40 years from the outcrop was designated the “recharge-influenced zone.” Wells within this zone would be expected to produce water that could be affected by nonpoint-source contamination.

Land-use maps depicting the aquifer system’s outcrop area are available from the Gloucester County Planning Department at a scale of 1:4,800 and were derived from aerial photographs taken in 1990. These maps are used for property-tax and transaction purposes and, at that scale, individual lots are resolvable. The land uses on these maps are divided into nine major categories: residential, manufacturing, transportation, trade, services, recreation, resource development, undeveloped, and unknown. These categories are further subdivided into a total of 88 specific land uses. The land use of greatest relevance to this study of nonpoint-source ground-water contamination is chemical-products manufacturing and petroleum refining. These industries have been present in the area for 40 to 50 years and are the likely source of contamination by organic chemicals. Many such industries are present in the study area, which has a long history of observed contamination (Fusillo and others, 1984). The land-use maps depicting the aquifer system’s outcrop area were digitized and a Geographical Information System was used to facilitate the determination of the land use at the origin of each flowpath evaluated by particle tracking. Each active model-cell face was the origin for 400 particles (a total of 2,400 particles per cell) used to “backtrack” the contributing flowpaths from each well studied.

CONTRIBUTING AREAS AND TRAVELTIMES

The simulated downdip limit of direct surficial recharge to the aquifer system within the study area, shown in figure 1B, is from 0.5 to 2 miles downdip from (southeast of) the upper aquifer’s outcrop area. This limit, based on simulation results, delineates the recharge-influenced zone and is consistent with observed regional ground-water quality. Chemical compounds related to human activities, such as volatile organic compounds (VOC’s), heavy metals, and nutrients, generally were not detected in water samples from wells completed in the aquifer system more than 1 mile downdip from the outcrop (Vowinkel and Battaglin, 1989a).

Many water-supply wells are within the recharge-influenced zone that could be vulnerable to nonpoint-source contamination. The contributing areas of three wells—15-069 (Greenwich Water Department #3), 15-348 (Greenwich Water Department #6), and 15-212 (Paulsboro Water Department #4)—were evaluated. All three wells are within about 1 mile of each other and are screened in the middle aquifer. In order for ground water from the closest part of the outcrop area to reach the well, it must flow through a leaky confining unit. All three of the wells were “strong” sinks—that is, all flow across the boundaries of the cell containing the well was into the cell.

Only part of the outcrop area contributes water to an individual well. Because chemicals are manufactured in the study area, VOC’s are found in the ground water as nonpoint-source contaminants. Figure 2 shows the contributing areas of the
Figure 2. Locations of wells, contributing areas, and areas of manufacturing land use.
selected wells determined by simulation of the ground-water-flow system, and the locations of manufacturing land use in the study area. The manufacturing land use is devoted predominantly to chemical production and petroleum refining. Inset A in figure 2 shows the simulated contributing area to well 15-069. Manufacturing land use is present at the northwestern end of this contributing area. Inset B in figure 2 shows the simulated contributing area to well 15-348. A small area of manufacturing land use is present within this contributing area. The three small, isolated areas extending into the Delaware River contribute to this well. Inset C in figure 2 shows the simulated contributing area to well 15-212. Manufacturing land use is present about 0.5 miles from the well and is within this contributing area.

The shapes of the contributing areas (fig. 2) are fairly irregular and do not closely resemble the conceptualized patterns, such as fixed-radii circles, truncated parabolas, or "keyholes," that are associated with some wellhead-protection schemes (U.S. Environmental Protection Agency, 1987). The proximity of these production wells to each other causes drawdown interference that results in the "nested" aspects shown in the simulation results.

The land use within the contributing areas was determined from the land-use maps and is compiled in tables 1, 2, and 3 for wells 15-069, 15-348, and 15-212, respectively. These tables include the number of particles simulated and traveltimes to the wells from each category of land use. Chemical-products manufacturing and petroleum-refining land uses are highlighted in each table.

The primary land uses (those contributing more than 100 particles) contributing water to well 15-069 (table 1) are undeveloped, residential, and agricultural. The average traveltimes from these land uses range from 21 years to 134 years. Of the 2,400 particles per cell used in the analysis, 50 are contributed from chemical-products manufacturing land use. The minimum travel time from the source of these particles is 51 years. The number of particles is only loosely related to the proportion of the flow to the well. The particles were assigned uniformly to each face of the model cell, but the contribution of flow from each face to the well is not uniform.

The primary land uses contributing water to well 15-348 (table 2) are residential, undeveloped, agricultural, and recreational. The average traveltimes from these land uses range from 41 to 157 years. Three of the particles that flow to the well originate from chemical-products manufacturing land use, with a minimum travel time of 109 years.

Petroleum refining is a primary land use contributing water to well 15-212 (table 3); this land use contributes 327 particles with a minimum travel time of 30 years. Other primary land uses are undeveloped, residential, transportation, and services. The average traveltimes from these land uses range from 61 to 94 years.

If particles from contributing areas that contain manufacturing land use are associated with traveltimes of less than 50 years, VOC contamination of the water in the receiving well is possible. Well 15-212 fits this scenario; a large number of particles that flow to this well originate from petroleum-refining land-use areas, with a minimum travel time of 30 years. This is consistent with observed water-quality data. VOC's detected in well 15-212 are listed in table 4. Much smaller numbers of particles that flow to the other two wells, 15-069 and 15-368, originate from manufacturing land-use areas, and minimum traveltimes are longer than 50 years. It is feasible to assume that insufficient time has elapsed for contamination to reach these two wells. This scenario also is consistent with observed data, as no VOC's have been detected at these wells. Future contamination can be predicted as follows: (1) The two wells containing water in which no VOC's have been detected are threatened with contamination because manufacturing land use is present within the contributing area and "contaminated" particles are "in route;" and (2) concentrations of VOC's in water from well 15-212, where VOC concentrations have thus far been low, probably will increase in the future because the average travel time from the manufacturing land-use area is 61 years, whereas the minimum is 30 years, indicating that additional contamination can be expected to appear in this well.
Table 1. Land uses of area contributing water to well 15-069

<table>
<thead>
<tr>
<th>Number of particles</th>
<th>Average travel time (yr)</th>
<th>Maximum travel time (yr)</th>
<th>Minimum travel time (yr)</th>
<th>General land-use category</th>
<th>Specific land use</th>
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<tbody>
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<td>652</td>
<td>44</td>
<td>262</td>
<td>8</td>
<td>Residential</td>
<td>Detached Single Family</td>
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<tr>
<td>12</td>
<td>20</td>
<td>56</td>
<td>9</td>
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<td>Semi-Attached Single Family</td>
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<td>3</td>
<td>46</td>
<td>56</td>
<td>30</td>
<td>Residential</td>
<td>Apartments</td>
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<td>152</td>
<td>169</td>
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<td>Group Quarters</td>
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<td>50</td>
<td>163</td>
<td>272</td>
<td>51</td>
<td>Manufacturing</td>
<td>Chemical Products</td>
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<td>4</td>
<td>75</td>
<td>86</td>
<td>68</td>
<td>Transportation</td>
<td>Automobile Parking</td>
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<td>16</td>
<td>26</td>
<td>8</td>
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<td>68</td>
<td>68</td>
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<td>Food</td>
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<tr>
<td>1</td>
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<td>20</td>
<td>20</td>
<td>Trade</td>
<td>Automobile, Aircraft, Boats</td>
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<tr>
<td>4</td>
<td>109</td>
<td>196</td>
<td>26</td>
<td>Trade</td>
<td>Eating and Drinking</td>
</tr>
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<td>1</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>Trade</td>
<td>Other Trade</td>
</tr>
<tr>
<td>8</td>
<td>34</td>
<td>86</td>
<td>24</td>
<td>Services</td>
<td>Personal Services</td>
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<td>200</td>
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<td>Services</td>
<td>Warehousing and Storage</td>
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<td>Services</td>
<td>Automobile Repair</td>
</tr>
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<td>7</td>
<td>23</td>
<td>26</td>
<td>21</td>
<td>Services</td>
<td>Other Repair</td>
</tr>
<tr>
<td>11</td>
<td>26</td>
<td>30</td>
<td>24</td>
<td>Services</td>
<td>Other Professional Services</td>
</tr>
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<td>47</td>
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<td>Services</td>
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<td>Miscellaneous Services</td>
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<td>8</td>
<td>Resources</td>
<td>Agriculture</td>
</tr>
<tr>
<td>4</td>
<td>83</td>
<td>100</td>
<td>68</td>
<td>Resources</td>
<td>Mining Activities</td>
</tr>
<tr>
<td>190</td>
<td>73</td>
<td>249</td>
<td>8</td>
<td>Undeveloped</td>
<td>Unused, Undeveloped</td>
</tr>
<tr>
<td>510</td>
<td>28</td>
<td>154</td>
<td>8</td>
<td>Undeveloped</td>
<td>Forest Areas</td>
</tr>
<tr>
<td>151</td>
<td>134</td>
<td>166</td>
<td>35</td>
<td>Undeveloped</td>
<td>Rivers, Streams, Creeks</td>
</tr>
<tr>
<td>305</td>
<td>50</td>
<td>131</td>
<td>23</td>
<td>Undeveloped</td>
<td>Wetlands</td>
</tr>
<tr>
<td>1</td>
<td>8</td>
<td>8</td>
<td>8</td>
<td>Unknown</td>
<td>Unknown</td>
</tr>
<tr>
<td>5</td>
<td>24</td>
<td>29</td>
<td>18</td>
<td>Unknown</td>
<td>Unknown</td>
</tr>
</tbody>
</table>

Table 2. Land uses of area contributing water to well 15-348

<table>
<thead>
<tr>
<th>Number of particles</th>
<th>Average travel time (yr)</th>
<th>Maximum travel time (yr)</th>
<th>Minimum travel time (yr)</th>
<th>General land-use category</th>
<th>Specific land use</th>
</tr>
</thead>
<tbody>
<tr>
<td>67</td>
<td>208</td>
<td>258</td>
<td>172</td>
<td>Unknown</td>
<td>From Pennsylvania</td>
</tr>
<tr>
<td>1,078</td>
<td>41</td>
<td>541</td>
<td>19</td>
<td>Residential</td>
<td>Detached Single Family</td>
</tr>
<tr>
<td>3</td>
<td>23</td>
<td>24</td>
<td>22</td>
<td>Residential</td>
<td>Semi-Attached Single Family</td>
</tr>
<tr>
<td>2</td>
<td>23</td>
<td>23</td>
<td>22</td>
<td>Residential</td>
<td>Apartments</td>
</tr>
<tr>
<td>1</td>
<td>174</td>
<td>174</td>
<td>174</td>
<td>Residential</td>
<td>Group Quarters</td>
</tr>
<tr>
<td>3</td>
<td>134</td>
<td>183</td>
<td>109</td>
<td>Manufacturing</td>
<td>Chemical Products</td>
</tr>
<tr>
<td>2</td>
<td>141</td>
<td>141</td>
<td>141</td>
<td>Transportation</td>
<td>Motor Vehicle Freight</td>
</tr>
<tr>
<td>6</td>
<td>107</td>
<td>124</td>
<td>57</td>
<td>Transportation</td>
<td>Automobile Parking</td>
</tr>
<tr>
<td>5</td>
<td>144</td>
<td>144</td>
<td>144</td>
<td>Trade</td>
<td>Furniture, Home Furnishings</td>
</tr>
<tr>
<td>1</td>
<td>79</td>
<td>79</td>
<td>79</td>
<td>Services</td>
<td>Other Professional Services</td>
</tr>
<tr>
<td>1</td>
<td>191</td>
<td>191</td>
<td>191</td>
<td>Services</td>
<td>Contract Construction</td>
</tr>
<tr>
<td>4</td>
<td>141</td>
<td>141</td>
<td>141</td>
<td>Services</td>
<td>Government Services</td>
</tr>
<tr>
<td>40</td>
<td>72</td>
<td>172</td>
<td>44</td>
<td>Services</td>
<td>Primary, Nursery Education</td>
</tr>
<tr>
<td>108</td>
<td>51</td>
<td>339</td>
<td>30</td>
<td>Recreation</td>
<td>Recreational Activities</td>
</tr>
<tr>
<td>238</td>
<td>121</td>
<td>634</td>
<td>46</td>
<td>Resources</td>
<td>Agriculture</td>
</tr>
<tr>
<td>14</td>
<td>118</td>
<td>192</td>
<td>106</td>
<td>Resources</td>
<td>Mining Activities</td>
</tr>
<tr>
<td>47</td>
<td>102</td>
<td>267</td>
<td>19</td>
<td>Undeveloped</td>
<td>Unused, Undeveloped</td>
</tr>
<tr>
<td>352</td>
<td>56</td>
<td>539</td>
<td>20</td>
<td>Undeveloped</td>
<td>Forest Areas</td>
</tr>
<tr>
<td>162</td>
<td>157</td>
<td>309</td>
<td>30</td>
<td>Undeveloped</td>
<td>Rivers, Streams, Creeks</td>
</tr>
<tr>
<td>266</td>
<td>145</td>
<td>357</td>
<td>43</td>
<td>Undeveloped</td>
<td>Wetlands</td>
</tr>
</tbody>
</table>
Table 3. Land uses of area contributing water to well 15-212

<table>
<thead>
<tr>
<th>Number of particles</th>
<th>Average travel time (yr)</th>
<th>Minimum travel time (yr)</th>
<th>General land-use category</th>
<th>Specific land use</th>
</tr>
</thead>
<tbody>
<tr>
<td>327</td>
<td>63</td>
<td>29</td>
<td>Residential</td>
<td>Detached Single Family</td>
</tr>
<tr>
<td>57</td>
<td>50</td>
<td>29</td>
<td>Residential</td>
<td>Semi-Attached Single Family</td>
</tr>
<tr>
<td>21</td>
<td>63</td>
<td>60</td>
<td>Residential</td>
<td>Mobile Homes</td>
</tr>
<tr>
<td>136</td>
<td>236</td>
<td>30</td>
<td>Manufacturing</td>
<td>Petroleum Refining</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>36</td>
<td>39</td>
<td>34</td>
<td>Transportation</td>
<td>Motor Vehicle Freight</td>
</tr>
<tr>
<td>155</td>
<td>84</td>
<td>30</td>
<td>Transportation</td>
<td>Automobile Parking</td>
</tr>
<tr>
<td>94</td>
<td>59</td>
<td>30</td>
<td>Trade</td>
<td>General Merchandise</td>
</tr>
<tr>
<td>66</td>
<td>58</td>
<td>30</td>
<td>Trade</td>
<td>Food</td>
</tr>
<tr>
<td>57</td>
<td>71</td>
<td>53</td>
<td>Trade</td>
<td>Automobile, Aircraft, Boats</td>
</tr>
<tr>
<td>54</td>
<td>81</td>
<td>30</td>
<td>Trade</td>
<td>Apparel and Accessories</td>
</tr>
<tr>
<td>3</td>
<td>88</td>
<td>76</td>
<td>Trade</td>
<td>Eating and Drinking</td>
</tr>
<tr>
<td>99</td>
<td>57</td>
<td>30</td>
<td>Trade</td>
<td>Other Trade</td>
</tr>
<tr>
<td>20</td>
<td>78</td>
<td>57</td>
<td>Services</td>
<td>Finance, Insurance, Real Estate</td>
</tr>
<tr>
<td>38</td>
<td>60</td>
<td>32</td>
<td>Services</td>
<td>Personal Services</td>
</tr>
<tr>
<td>162</td>
<td>61</td>
<td>30</td>
<td>Services</td>
<td>Warehousing and Storage</td>
</tr>
<tr>
<td>54</td>
<td>228</td>
<td>50</td>
<td>Services</td>
<td>Government Services</td>
</tr>
<tr>
<td>22</td>
<td>64</td>
<td>55</td>
<td>Services</td>
<td>Miscellaneous Services</td>
</tr>
<tr>
<td>10</td>
<td>564</td>
<td>463</td>
<td>Recreation</td>
<td>Recreational Activities</td>
</tr>
<tr>
<td>322</td>
<td>69</td>
<td>29</td>
<td>Undeveloped</td>
<td>Unused, Undeveloped</td>
</tr>
<tr>
<td>288</td>
<td>83</td>
<td>30</td>
<td>Undeveloped</td>
<td>Forest Areas</td>
</tr>
<tr>
<td>32</td>
<td>175</td>
<td>61</td>
<td>Undeveloped</td>
<td>Rivers, Streams, Creeks</td>
</tr>
<tr>
<td>156</td>
<td>94</td>
<td>62</td>
<td>Undeveloped</td>
<td>Wetlands</td>
</tr>
</tbody>
</table>

Table 4. Volatile organic compounds detected in well 15-212

[Concentrations shown are highest concentrations detected in samples collected on 11-30-82, 10-22-86, 4-23-87, 11-5-87, 2-11-88, and 8-10-88; μg/L, micrograms per liter]

<table>
<thead>
<tr>
<th>Compound</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bromoform (total)</td>
<td>0.6 μg/L</td>
</tr>
<tr>
<td>1,2-Dichloropropane (total)</td>
<td>0.4 μg/L</td>
</tr>
<tr>
<td>Chlorodibromomethane (total)</td>
<td>.4 μg/L</td>
</tr>
<tr>
<td>Chloroform (total)</td>
<td>.2 μg/L</td>
</tr>
<tr>
<td>1,2-Dichloroethane (total)</td>
<td>.9 μg/L</td>
</tr>
<tr>
<td>Tetrachloroethylene (total)</td>
<td>.2 μg/L</td>
</tr>
<tr>
<td>Toluene (total)</td>
<td>.2 μg/L</td>
</tr>
</tbody>
</table>
CONCLUSIONS

A ground-water-flow model that incorporates particle tracking with high-resolution land-use data has been used to investigate the possible extent of nonpoint-source contamination at a regional level and to simulate the source and timing of contamination at production wells. Results are consistent with field data, indicating that the method is useful in the analysis of nonpoint-source ground-water contamination.

The method used to perform the analyses outlined in this report could be applied easily to other locales, provided that a finely discretized ground-water-flow model and a detailed land-use data base are available. Although either of these resources may not be considered commonplace, ground-water-flow models produced as part of many U.S. Geological Survey cooperative studies, such as those of the Regional Aquifer-Systems Analysis (RASA) program, could be used in a similar manner with an appropriate land-use data base.

REFERENCES


Pollock, D.W., 1988, Semianalytical computation of path lines for finite-difference models: Groundwater, v. 26, no. 6, p. 743-750.


Vowinkel, E.F., and Battaglin, W.A., 1989a, Hydrogeological, well construction, and land-use factors that can affect the evaluation of regional ground-water quality, in Ragone, S.E., ed., Proceedings of the International Association of Hydrological Sciences, IAHS publication no. 182, p. 69-77.


Vulnerability of Water from Public Supply Wells to Contamination by Pesticides, Potomac-Raritan-Magothy Aquifer System, New Jersey Coastal Plain

By Eric F. Vowinkel

Abstract

A numerical rating model used in conjunction with hydrogeologic, land-use, and water-quality data stored in a geographic information system was developed to rank 558 public supply wells screened in the Potomac-Raritan-Magothy aquifer system in the New Jersey Coastal Plain into groups of high, medium, and low vulnerability to contamination by pesticides. The vulnerability of water from public supply wells to contamination by pesticides is defined by variables describing the (1) sensitivity of the aquifer to contamination and (2) intensity of pesticide use in areas where the aquifer is sensitive. The results of the model indicated that 305 wells were of low vulnerability, 237 were moderately vulnerable, and 16 were highly vulnerable to contamination. Because analyses for pesticides in water samples are scarce, the concentration of nitrate in water samples was used as a surrogate to develop and test the accuracy of the model. Results of statistical tests indicate that the concentration of nitrate is a significant indicator of aquifer sensitivity, pesticide-use intensity, and the presence of pesticides in ground water. Results of the rating model indicate that water from only 1 of the 138 sampled wells that were ranked as low vulnerability contained nitrate as nitrogen in concentrations larger than 0.5 milligrams/L. Concentrations of nitrate in water samples were significantly larger in the medium- and high-vulnerability groups than in the low-vulnerability group.

INTRODUCTION

Regulations established by the U.S. Environmental Protection Agency (USEPA) will require water purveyors to monitor samples from public supply wells for pesticides on a quarterly basis beginning in 1994. Waivers for monitoring of pesticides in water samples can be granted in two instances: (1) if the part of the aquifer from which the water is withdrawn is insensitive to contamination by pesticides, or (2) if pesticides are not used in the area near the wellhead where the aquifer is sensitive to contamination (J.B. Louis, New Jersey Department of Environmental Protection and Energy, written commun., 1993). The U.S. Geological Survey (USGS) is developing a geographic information system (GIS) data base in cooperation with the New Jersey Department of Environmental Protection and Energy (NJDEPE) to provide data on the vulnerability of water from public supply wells to contamination by pesticides. This paper demonstrates the use of the GIS data base and a numerical rating model to rank the 558 known public supply wells screened in the Potomac-Raritan-Magothy aquifer system, the most widely used aquifer system for public supply withdrawals in New Jersey, into groups of low, medium, and high vulnerability to pesticide contamination.

The hydrogeologic framework of (Zapecza, 1989) and regional ground-water flow in (Martin, 1990) the New Jersey Coastal Plain are well documented. The sediments of the Potomac Group and Raritan and Magothy Formations of Cretaceous age underlie the entire New Jersey Coastal Plain and crop out in a narrow 5- to-16-km-wide strip of land covering

1 U.S. Geological Survey, West Trenton, N.J. 08628
about 1,000 km² from Raritan Bay to Delaware Bay (fig. 1). The Potomac-Raritan-Magothy aquifer system consists of five hydrogeologic units—three aquifers, designated as lower, middle, and upper; and two confining units. The Merchantville Formation and Woodbury Clay, which overlies the aquifer system, is the most extensive confining unit in the Coastal Plain. A long-term water budget for the Coastal Plain under unstressed conditions consists of about 112 cm/yr of precipitation, 51 cm/yr of streamflow, and 61 cm/yr of evapotranspiration. In 1985, withdrawals from public supply wells (fig. 1) screened in the aquifer system were about 6.9 x 10⁶ m³/d.

Types of land uses and land cover in the outcrop area of the aquifer system are diverse. In the early 1970s, the area consisted of about 49 percent urban land (25 percent residential and 24 percent urban-nonresidential), 19 percent agricultural land, and 32 percent undeveloped forests and wetlands. Some areas that were agricultural and undeveloped during the 1970s are now urban areas. Because ground water moves slowly, however, the effects of land use on ground-water quality probably are more closely related to previous rather than current land uses.

Pesticide use in various land-use areas in was estimated from available data collected as part of the NJDEPE's Pesticide Control Program (PCP). Most of the agricultural land is cropland, with smaller amounts of pasture and orchards. The amount of active pesticidal ingredients applied in 1991 in agricultural areas in or near the outcrop area of the aquifer system is estimated to be about 70,000 kg at an average rate of about 2.5 kg/km². The pesticides used in the largest amounts were sulfur, metolachlor, chlorothalonil, atrazine, captan, dichlorpropene, and linuron. Golf courses also are a potential source of pesticide contamination to ground water. In 1990, reported pesticide use at nine golf courses located in or near the outcrop area was about 6,000 kg at an average rate of about 11.2 kg/km². The pesticides used in the largest amounts on golf courses were thiram, chlorothalonil, propamocarb, and iprodione. Pesticide use in residential and urban-nonresidential areas is reported to the PCP by commercial lawn-care companies, but estimation of application rates is difficult because data on applications by homeowners are unavailable. Pesticide-use rates may be larger in some residential areas than those in agricultural areas (Roy Myer, New Jersey Department of Environmental Protection and
The most commonly used pesticides for lawn care in New Jersey in 1990 were 2,4-D, MCPP and pendimethalin.

METHODS OF INVESTIGATION AND DATA-BASE DEVELOPMENT

The vulnerability of an aquifer to contamination by pesticides is defined by (1) the sensitivity of the aquifer to contaminants from the land surface and (2) the intensity of pesticide-use activities in areas where the aquifer is sensitive to contamination. The sensitivity of an aquifer is defined by its physical properties that determine whether contaminants can enter the ground water, whether they can be transported along a flow path, and whether the ground water is older than when pesticides were first applied at the land surface in the recharge area. For example, relatively young ground water in the outcrop area near the surface-water divide that is beneath soils containing little organic matter and less than 30 m from the land surface is more sensitive to potential sources of pesticides than ground water 2 km downdip from the outcrop area where the ground water recharged the aquifer system more than 50 years ago. Similarly, the intensity of pesticide use is not uniform among land-use areas; it is assumed that the potential for contamination of ground water is greater in recharge areas that are agricultural, golf courses, or residential than in those that are undeveloped.

Hydrogeologic, land-use, and water-quality data were stored in a GIS data base (table 1) to allow for spatial analysis of the different types of data. The numerical vulnerability model ranks wells on the basis of selected variables to describe aquifer sensitivity and intensity of pesticide use in areas where the aquifer is sensitive to contamination. The sensitivity and intensity variables were coded so that the scores for the sensitivity of the aquifer and intensity of pesticide increased with the vulnerability to contamination by pesticides. Each sensitivity and intensity variable was coded from a low of 0 to a high of 5, with 3 being moderate.

The data base and rating model serve as a means for a generalized, regional assessment of vulnerability for each well. Development of a groundwater flow model to determine the zone of influence of each well or to locate point sources of pesticide use that potentially could affect the quality of water in each well is beyond the scope of this project. Some of the variables used in the model may double-account for certain factors; in recognition of this problem, the model is being refined as the project progresses.

Statistical procedures used to compare distributions of variables among groups include the Kruskal-Wallis test, Tukey's multiple comparisons test, and discriminant analysis. Discriminant analysis with ranked variables was used to determine those variables that best describe the presence of a contaminant in a concentration greater than or less than a given level. Relations among independent and dependent variables were considered significant at an alpha equal to or less than 0.05. Boxplots are used to compare the entire spread of data and percentiles by groups. Statistics were not computed for groups containing fewer than five cases.

Because analyses for pesticides were available for water samples from less than 5 percent of the public supply wells screened in the aquifer system, a surrogate was needed to test the vulnerability of a well to contamination by pesticides. The surrogate had to be (1) available in sufficient numbers to allow meaningful predictions and (2) an indicator of the presence of pesticides, the sensitivity of the aquifer system, and the intensity of pesticide use. Nitrate concentrations in water samples satisfied both these requirements. Water-quality analyses for nitrate in samples collected by the USGS from sampling ports near the wellhead were available for statistical analysis for 267 of the 558 public supply wells screened in the aquifer system.

A significant relation exists among concentration of nitrate, presence of pesticides, and well depth in water samples from 81 shallow wells (depth to top of the screened interval less than 30 m below land surface) in agricultural areas of the Coastal Plain (Louis and Vowinkel, 1989). The concentration of nitrate as nitrogen (as N) in water samples was significantly larger (p=0.003) in wells in which pesticides were present than in wells in which pesticides were absent (fig. 2A); the 25th-percentile nitrate concentration in samples containing a pesticide was about 6 mg/L. Results of discriminant analysis indicate that concentrations of nitrate and the frequency of pesticide detection decreased with well depth. Pesticide concentrations ranged from 0.1 to 13 ug/L, and water from 1 of 81 wells contained a pesticide in a concentration that exceeded a USEPA maximum contaminant level or health advisory. The pesticides most commonly detected were carbamate (aldicarb and carbofuran) insecticides and triazine (atrazine and simazine) and acetanilide (alachlor and metolachlor) herbicides. These compounds are more
Table 1. Description of sensitivity and intensity variables, assumptions, and numerical scores used in the numerical ranking model to determine the vulnerability of water from public supply wells screened in the Potomac-Raritan-Magothy aquifer system to contamination by pesticides

[USGS, U.S. Geological Survey; NWIS, National Water Information System; SCS, U.S. Soil Conservation Service; NJDEPE, New Jersey Department of Environmental Protection and Energy; PCP, Pesticide Control Program; UNO, undeveloped; RES, urban-residential; URB, urban-nonresidential; AGR, agricultural; <, less than; ≤, equal to or less than; -, no numerical score]

<table>
<thead>
<tr>
<th>Variable and source of data</th>
<th>Assumptions used for ranking score</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aquifer-sensitivity variables (Variables 3, 4, and 5 applied only to wells in the outcrop area):</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. Location of well relative to the outcrop area (USGS/NWIS)</td>
<td>Effects of land uses on ground water quality are greater in the outcrop area than downdip from the outcrop area (see fig. 2B)</td>
<td>Down-dip</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>ln</td>
</tr>
<tr>
<td>2. Distance of the well from the outcrop area, in meters (Zapeza, 1989)</td>
<td>Effects of land uses decrease as the distance from the outcrop or recharge area increases</td>
<td>≥1,600</td>
<td>1,200</td>
<td>800</td>
<td>400</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>3. Distance of the well from the surface-water divide, in meters (USGS)</td>
<td>Ground-water flow paths are shortest and water is youngest near the surface-water divide and the age of the ground water increases with distance from the divide</td>
<td>≥1,600</td>
<td>1,200</td>
<td>800</td>
<td>400</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>4. Lower extreme of soil-organic-matter content, in percent (SCS)</td>
<td>Sorption of some pesticides increases as the amount of organic matter in the soil increases</td>
<td>≥2.0</td>
<td>-</td>
<td>-</td>
<td>1.0</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>5. Depth to the bottom of the well, in meters (USGS/NWIS)</td>
<td>The depth of the well is a measure of the vertical distance a contaminant has traveled; concentration decreases with well depth</td>
<td>≥150</td>
<td>120</td>
<td>90</td>
<td>60</td>
<td>30</td>
<td>0</td>
</tr>
<tr>
<td>Pesticide-use-intensity variables (Variables applied only to wells in the outcrop area):</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. Predominant land use within an 800-meter-radius buffer zone of the wellhead (USGS; Fegeas and others, 1983)</td>
<td>The land use with the largest areal extent surrounding the well has the greatest effect on the quality of water in the well. Agricultural areas have a greater effect on ground-water quality than undeveloped, urban-residential, and urban-nonresidential areas (see fig. 2C)</td>
<td>UND</td>
<td>URB</td>
<td>-</td>
<td>RES</td>
<td>-</td>
<td>AGR</td>
</tr>
<tr>
<td>2. Distance of the well from nearest agricultural land, in meters</td>
<td>The effect of agricultural land on ground-water quality is greatest in areas where agricultural land is near the wellhead</td>
<td>≥1,600</td>
<td>1,200</td>
<td>800</td>
<td>400</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>3. Distance of the well from the nearest golf course, in meters (NJDEPE/PCP)</td>
<td>The effect of pesticide and nitrate use on water quality decreases as the distance of the well from the golf course increases</td>
<td>≥1,600</td>
<td>1,200</td>
<td>800</td>
<td>400</td>
<td>1</td>
<td>0</td>
</tr>
</tbody>
</table>
soluble in water than the organochlorine insecticides that are measured in samples and reported by water purveyors to Federal and State agencies. The model assumes a similar relation among the presence of pesticides, nitrate concentration, and well depth in other land-use areas.

Variables used to describe the sensitivity (table 2) of the aquifer system to contamination were (1) location of the well relative to the outcrop area, (2) distance of the well from the outcrop area if the well is screened downdip from the outcrop, (3) percentage of organic matter in the soils at the wellhead, (4) distance of the well from the surface-water divide, and (5) depth of the well screen below land surface. The best predictor of nitrate concentration in ground water is the location of the well relative to the outcrop area; the nitrate concentrations in water samples from wells are significantly larger (p=0.003) in the outcrop area than downdip from the outcrop area, where the concentrations rarely are greater than 0.1 mg/L (fig. 2B). All but one of the wells downdip from the outcrop area containing water with “outlier” nitrate concentrations are less than 800 m from the outcrop area. For wells in the outcrop area, negative relations between nitrate concentration and the percentage of soil organic matter and between nitrate concentration and distance from the surface-water divide were expected. Results of discriminant analysis indicate that nitrate concentration is significantly related to well depth but not to percentage of organic matter or distance of the well from the surface-water divide.

Figure 2. Distribution of concentrations of nitrate in water samples from wells screened in the Potomac-Raritan-Magothy aquifer system by the (A) presence or absence of pesticides in the water sample in agricultural areas (modified from Louis and Vowinkel, 1989, fig. 3); (B) location of the well relative to the outcrop area; and (C) predominant land use within an 800-meter-radius buffer zone of shallow wells (modified from Vowinkel, 1991, fig. 5).
Table 2. Number of public supply wells and number of wells sampled for nitrate in the Potomac-Raritan-Magothy aquifer system, by groups of aquifer sensitivity and pesticide-use intensity

<table>
<thead>
<tr>
<th>Pesticide-use intensity</th>
<th>Aquifer sensitivity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Low</td>
</tr>
<tr>
<td>Low</td>
<td>305/138</td>
</tr>
<tr>
<td>Medium</td>
<td>0/0</td>
</tr>
<tr>
<td>High</td>
<td>0/0</td>
</tr>
</tbody>
</table>

Variables used to describe the intensity of pesticide use (table 2) near a well in an area that is sensitive to contamination were (1) predominant land use within an 800-m-radius buffer zone of the well, (2) distance of the well from the nearest parcel of agricultural land, and (3) distance of the well from the nearest golf course. Results of discriminant analysis indicate that the first two variables are significantly associated with the concentration of nitrate in water samples from wells in the outcrop area. A significant relation exists between the concentration of nitrate in shallow ground water and the predominant land use (fig. 2C) within an 800-m-radius buffer zone of the wellhead (Vowinkel, 1991; Vowinkel and Battaglin, 1989). Nitrate was rarely detected in ground water in undeveloped areas, where use of nitrate and pesticide is low. Concentrations of nitrate in shallow ground water in agricultural areas exceeded 10 mg/L in more than 33 percent of the wells in agricultural areas. Concentrations of nitrate in shallow ground water in residential and nonresidential urban areas typically were between those in shallow ground water in undeveloped and urban areas.

In some cases, outlier concentrations of nitrate were present in water from wells in predominantly undeveloped and residential areas. A closer examination of the results from well sites associated with outlier nitrate concentrations indicates that the wells are near agricultural areas but agriculture is not predominant. A significant negative relation exists, however, between nitrate concentration and the distance of the well from agricultural areas. As a result of these findings, agricultural areas were assigned the highest pesticide-use intensity, followed by golf courses, residential areas, urban-nonresidential areas, and undeveloped areas. Also, it was assumed that as the distance from a golf course increases, the potential effects of pesticide use on ground-water quality decrease.

RESULTS OF VULNERABILITY ANALYSIS

The model was used to group 558 public supply wells into 9 subgroups on the basis of sensitivity of the aquifer system and the intensity of pesticide use where the aquifer is sensitive to contamination (table 2). The results of the model indicated that 305 wells (55 percent) were of low vulnerability to contamination by pesticides because both the aquifer sensitivity and pesticide-use intensity are low. In this group, all the wells are more than 0.8 km downdip from the outcrop area. Only 16 wells (3 percent) were in areas where both the aquifer sensitivity and pesticide-use intensity are high; these wells typically are less than 30 m deep and in predominantly agricultural areas. The remaining 237 wells were identified as moderately vulnerable. The locations of the public supply wells are shown in figure 1, in which the wells are identified as having low, moderate, or high vulnerability to contamination by pesticides.

Concentrations of nitrate in water from wells were compared among the 9 subgroups (fig. 3); the number of water samples in each group is listed in table 2. The median concentration of nitrate (as N) in water samples from wells in the low-vulnerability group (low sensitivity and low intensity) was less than 0.1 mg/L and the concentration was larger than 0.5 mg/L in 1 of 138 public supply wells (0.07 percent). The spread of nitrate concentrations was greatest in wells grouped as moderate or high sensitivity and moderate or high intensity. The median nitrate concentration in water samples was largest in the high-vulnerability group (high sensitivity and high intensity); however, results of a Tukey’s multiple comparisons test indicate no significant difference in concentrations between the moderate- and high-vulnerability groups.

Assignment of the 41 wells identified as having high sensitivity and low intensity to a vulnerability group was subjective. These were shallow wells in predominantly undeveloped areas that were not near an agricultural area or a golf course. Because the pesticide-use intensity near these wells is low, the wells could be ranked as low vulnerability; however, because the data base used to quantify land use within an 800-m-radius buffer zone of a well contained data from the early 1970's, land-use changes since the 1970's potentially could affect the quality of water in the wells. Although nitrate concentrations in water from these wells were low, the wells were rated.
conservatively as moderately vulnerable to contamination by pesticides.

The accuracy of the numerical rating model to assign nitrate concentrations to the low-, medium-, and high-vulnerability groups was good. Because the presence of pesticides and concentrations of nitrate in ground water are related, the numerical rating model also is assumed to be applicable to the determination of vulnerability of water from wells to contamination by pesticides. The best predictors of nitrate concentration were the location of the well relative to the outcrop area, the predominant land use surrounding the well, and the distance of the well from agricultural land. The percentage of the organic-matter content of the soil may be a good predictor of potential pesticide contamination but was not effective for classifying nitrate concentration.

Model limitations result from the following assumptions made in the analysis: (1) the solubility of all pesticides in water is similar to that of nitrate, (2) pesticides are applied uniformly in agricultural and residential land-use areas, (3) the relation among concentration of nitrate, presence of pesticides, and well depth in agricultural areas is similar to that in other land-use areas, and (4) the various scales of the different data layers in the GIS do not affect the results of the statistical analyses. Because of these limitations, the rating model can be used only for a preliminary assessment of the potential vulnerability of water from public supply wells to contamination by pesticides. The limitations are being addressed as the project develops. The validity of the rating model will be assessed in the future by sampling a subset of the wells in each of the three vulnerability groups for selected pesticides and other water-quality constituents that may be predictors of pesticide contamination of ground water; expected and observed results will be compared.

**SUMMARY**

The vulnerability of water from public supply wells to contamination by pesticides is defined by variables describing the (1) sensitivity of the aquifer to contamination and (2) intensity of pesticide use in areas where the aquifer is sensitive. The results of the model indicated that 305 wells were of low vulnerability, 237 were moderately vulnerable, and 16 were highly vulnerable to contamination. Because analyses for pesticides in water samples are scarce, the concentration of nitrate in water samples was used as a surrogate to develop and test the accuracy of the model. Results of statistical tests indicate that the concentration of nitrate is a significant indicator of aquifer sensitivity, pesticide-use intensity, and the presence of pesticides in ground water. Results of the rating model indicate that water from only 1 of the 138...
sampled wells that were ranked as low vulnerability contained nitrate as nitrogen in concentrations larger than 0.5 mg/L. Concentrations of nitrate in water samples were significantly larger in the medium- and high-vulnerability groups than in the low-vulnerability group.

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A Review of Methods for Assessing the Potential for Regional Ground-Water Contamination

By David R. Soller

Abstract

The potential for ground-water contamination, or the sensitivity of an area to ground-water contamination, can be estimated by a quantitative, deterministic model that predicts fate and transport of water and contaminants locally, or by a broad, regional qualitative model. Although regional models do not predict ground-water contamination at specific sites as accurately as do the local models, the former are useful tools for regional planning and research. All regional models depict relative contamination potential. Some models focus on contamination potential of ground water in aquifers, either at the land surface or confined beneath low-permeability sediments, whereas other models focus on ground water at the unconfined water table. For a given area, the focus of ground-water protection efforts will determine which models are most appropriate. Some regional models use dimensionless numbers and weighting factors to derive a relative measure of contamination potential, whereas others assemble source data into a composite map and rank the resulting map units for contamination potential according to a set of rules. Both approaches have certain advantages. However, because most contamination potential maps in the area considered (Central United States) show roughly similar patterns of contamination potential, some models may be more practical than others. For example, if simple models give results similar to models requiring cumbersome numeric manipulation of data, there is little justification for the effort needed to execute the more complex model.

Availability of information required by a model also should determine its utility. Regional, stochastic models that provide actual, not relative, predictions of contamination potential are needed. Those models should consider the uncertainty in source information in order to estimate contamination potential with specified levels of uncertainty.

INTRODUCTION

Contamination of ground-water resources has become an issue of national concern. Many models for assessing the potential for ground-water contamination have been proposed and used. Two general approaches exist: farm- or field-scale deterministic models that predict rate of transport and fate of specific chemicals, and regional models that show general trends of the potential for ground-water contamination. Here, regional refers to areas larger than a local community or farm (for example, a county or a State). These two categories of models have little in common.

Deterministic models that require many quantitatively defined variables are developed to estimate rates and patterns of contaminant migration as precisely as possible (see Ertel, 1990, for a summary of models), at least for the locality where the model was developed. Given the large data requirements of some deterministic models, their applicability to a wide variety of localities can be limited. Also, these models have not been, and perhaps cannot be, applied to areas larger than farm-scale with notable success, because they require variables that are not available regionally and because it is more difficult to characterize precisely the variability of geologic materials and resulting ground-water flow regionally than it is locally.

Although valuable data concerning water and contaminant movement are provided by site studies, a regional perspective is required by planners and researchers who must deal with geologic and hydrologic features not limited to specific localities or sites.

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Detailed, local information is necessary for precise characterization of an area or for remedial engineering but is not particularly helpful or efficient for identifying larger areas with potential contamination problems. Regional models allow for rapid contamination potential mapping of large areas by use of existing data. For practical reasons, such as limited availability of data, regional models must rely on a few generalized, qualitative variables.

Regional models are known to be inaccurate predictors of local ground-water contamination, because only the broad, regional nature of the geologic and hydrologic framework can be characterized in these models. However, there is at present no alternative that will predict contamination with the reliability of highly detailed deterministic models. Regulators and policymakers must, by necessity, contend with the shortcomings of regional models. Potential advances in quantifying regional information and in developing stochastic models that more accurately predict contamination could significantly reduce the uncertainty of the information upon which regulatory and policy decisions are based. Development of new approaches that reduce this uncertainty would be a significant scientific advance as well as an economic benefit to society.

In this paper, selected regional models are described and compared, and their predictive abilities are addressed. This discussion is limited to models that have been applied to a specific area—the glaciated central United States—to simplify the model comparisons. The importance of geologic framework is emphasized here, because geologic materials dictate hydrogeologic properties upon which interpretations of the availability of ground-water and potential for its contamination are based.

REGIONAL MODELS

In order to address the potential for regional ground-water contamination, a model may focus, for example, on characteristics of the soil, the geologic materials at and above the unconfined water table, or on the larger part of the geologic framework containing buried aquifers. A model's focus significantly affects the utility of maps produced by the model. A model focusing on the soil or vadose zone cannot adequately characterize the contamination potential of confined aquifers.

Models address the qualitative manipulation of data and relative ranking of contamination potential map units in one of two general ways: Some translate the data into dimensionless numbers for manipulation into a relative contamination potential index value, whereas others classify the data into map units of relative contamination potential without representing the data with numbers. The most commonly used model is "DRASTIC," an acronym for the model's elements, or factors (depth to water, net recharge, aquifer media, soil media, topography, impact of the vadose zone media, and hydraulic conductivity of the aquifer). DRASTIC maps have been generated for individual counties and states across the United States. It was developed by a committee using the Delphi approach to specify relative significance for each factor. A user's manual (Aller and others, 1987) provides descriptions of common hydrogeologic settings across the United States and expected values and the specified "weight," or multiplier, for each factor. With this information, or with actual information for a local area, DRASTIC scores can be calculated for each hydrogeologic setting and a DRASTIC map generated. Hydrogeologic settings can be defined to include buried aquifers, although the model does not address them as effectively as do other models (Berg and Kempton, 1984). Soller (1992) notes deficiencies in the model and, particularly, in the inconsistent manner in which it has been applied by different modelers. As with all regional models, DRASTIC was designed primarily as a regional tool for prioritization, or screening, to indicate areas that are relatively sensitive to contamination and, therefore, in need of more detailed mapping and evaluation or monitoring.

A model developed for the Wisconsin Department of Natural Resources (WDNR) was used to generate a statewide contamination potential map (Schmidt, 1987). In this model, all unconfined ground water is considered, whether in permeable, sandy surface aquifers or in low-permeability till. Ground water in confined aquifers is not addressed. Data for the factors (soil texture, type of surficial deposits, depth to the water table, type of bedrock, and thickness of glacial drift) are assigned an arbitrary numbers based on perceived importance. Like DRASTIC, these numbers are weighted and summed to produce the contamination potential score. Unlike DRASTIC, hydrogeologic settings are not delineated; rather, maps of each factor are intersected in a Geographic Information System (GIS)
to produce a composite map. This map does not have distinct map units but has color gradations representing changes in relative contamination potential.

For Minnesota, a similar approach was used to map the potential for ground-water contamination to depths including the uppermost aquifer (Porcher, 1989). Like the WDNR approach, factors such as aquifer materials, recharge potential, soil materials, and vadose-zone materials were ranked for their effect on the potential for ground-water contamination and combined in a GIS to yield a composite relative contamination-potential index.

In contrast to the numeric approaches for ranking map areas, a method to map areas of potential ground-water contamination developed by Berg and Kempton (1984) of the Illinois State Geological Survey (ISGS) orders map units in a hierarchy from relatively low to high contamination potential. Also in contrast to the numeric models, the ISGS model relies solely on the textural character of the three-dimensional geologic framework to a specified depth. The ISGS maps consider aquifers. This approach has been modified in cooperation with the U.S. Geological Survey (USGS) to address contamination potential of multi-State areas based on information less detailed than was available in Illinois (Soller and Berg, 1992).

Like the ISGS-USGS maps, a GIS-based map produced for Michigan (Lusch and others, 1992) also addresses ground water in aquifers. Relative soil permeability, presence of fine-grained materials within the upper 40 ft, and soluble (and therefore, presumably, permeable) bedrock within 50 ft of land surface are considered. Documentation on the model is limited, but it appears that aquifers deeper than 50 ft are not considered.

Pettyjohn and others (1991) offer the only national appraisal of the potential for ground-water contamination. They emphasize contamination from shallow injection wells and, therefore, address aquifiers. The report provides only individual page-size maps of each State, so each State must be viewed in isolation. Regional integration of map information, across all States and with a common map scale, would be invaluable.

**COMPARISON OF CONTAMINATION POTENTIAL MAPS**

Lack of adequate information is a restraint to the development of any model. Modelers are compelled to use only the more commonly available types of data and the models are thereby limited in their ability to predict contamination. Some data significant in predicting movement of water and contaminants (such as the presence of macropores, or organic carbon content of soils) are less readily available, and, therefore, not used in regional models. Data on depth to the water table are not commonly available yet are required by some models (the DRASTIC and the WDNR model, for example). Schmidt (1987), in a summary of the WDNR map, notes that depth to water table had the least influence on the model and was the least reliable component of information because it had to be estimated (not measured) for most of the state. Models that address buried aquifers must consider subsurface geologic units. This consideration may require detailed data that are scarce or difficult to acquire. For areas where such data are unavailable, the model must be able to make certain inferences on subsurface units on the basis of other criteria (overall thickness of deposits, for example) or to note on the map the lack of data for those areas (Lusch and others, 1992; Soller and Berg, 1992).

Regional maps can depict contamination potential by assigning a rank to an area with mapped boundaries, such as an alluvial valley, or by combining model factors in a GIS to produce map units unrelated to any single factor mappable at land surface (such as soil). The DRASTIC model represents the first case, and the WDNR and Minnesota models represent the second. The ISGS and USGS-ISGS maps are somewhat intermediate: Map units represent a combination of several factors but retain the general configuration of surfacemappable units. The WDNR approach shows that contamination potential is a function of many factors and limits the effect of any one factor by producing a map that almost represents a raster image of contamination-potential scores across the State. This approach limits the tendency to use contamination-potential scores literally for identifiable areas, such as a specific alluvial valley. On the other hand, retention of map boundaries, such as alluvial valleys, from the source data can allow a user to reinterpret the map for related purposes. Because the three-dimensional geologic framework can be derived from the ISGS and USGS-ISGS maps, they can be used to identify, for example, aquifer recharge areas or thick areas of till overlying shale that could serve as a waste repository. DRASTIC maps cannot be reinterpreted as readily, because source information is reduced to a single, dimensionless number.
There are general similarities among the contamination-potential maps. The most important similarity is also the most important information on these maps—the differentiation of relatively high- and low-contamination-potential areas. Minor differences in the ranked contamination potential for any area among the maps are commonly meaningless because the models that generated the maps address more or less the same issue by using generalized data and assumptions based on expert opinion, not statistical verification. There are, of course, mapped areas where significant differences in ranked contamination potential occur. For areas covered by till and underlain by a buried aquifer, the WDNR model would likely assign a low contamination potential to the area because of the till cover. In contrast, the ISGS model would assign a relatively high or a moderate rating, depending on depth of the buried aquifer. A DRASTIC map might consider the buried aquifer and assign a higher rating; however, Soller (1992) noted a serious inconsistency with which data, and especially buried aquifers, were treated by persons producing DRASTIC maps.

The choice of an appropriate model may be based on many criteria, including the following. First, what resource is to be addressed—ground water in aquifers or unconfined, shallow ground water in both surface aquifers and low-permeability materials? Second, what is the distribution and quality of information shown on the model-generated map? The simpler models (for example, ISGS) yield maps similar to those from more intricate models, such as DRASTIC (which involve numeric manipulation of many types of data). In many cases, input data for DRASTIC are not even available, and estimated or standard values must be substituted. It is logical to suggest that simpler models, with appropriate factors selected, in part, by the distribution and quality of available data, would be preferable.

FUTURE EVOLUTION OF REGIONAL MODELS

Maps of regional ground-water contamination potential are best used only as qualitative tools, in part because of the sparseness of regional data or because of concern about the reliability (the uncertainty) of the data. With some exceptions (Halliday and Wolfe, 1991), these models do not consider the areal distribution of contaminant sources or other potentially relevant factors, such as precipitation. If these factors are considered, qualitative maps of ground water "vulnerability" to contamination from known sources can be produced. Some studies (Curry, 1987; Nielsen and Lee, 1987; Banton and Villeneuve, 1989; Baker, 1990) have assessed the ability of contamination-potential maps to predict actual contamination incidents or to approximate the results of deterministic models applied to detailed data at local sites. Results have not been encouraging, in part because regional models from which the maps are derived do not consider all factors pertinent to ground-water contamination. Also, regional water-quality and contaminant data may not be of sufficiently high quality and density to permit a regional, statistically valid assessment of contamination.

Regional contamination-potential maps might prove to be reasonably good predictors of actual contamination incidents. Statistical analysis provides the means to test these maps to determine their predictive abilities. However, spatial statistical analysis of such maps is inherently difficult. Lack of an adequate data base on ground-water quality contributes to the difficulty in testing the utility of these maps. Despite these problems, the science must advance beyond the current qualitative approach to stochastic models of the probability of ground-water contamination. New models need to consider the uncertainty of source information if they are going to provide estimates with specified levels of uncertainty. Estimates of contamination probability qualified by a measure of uncertainty will lead to more informed decisionmaking and more efficient management and regulation of our natural resources.

REFERENCES


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Hydrologic and Geochemical Factors affecting Metal Contaminant Transport in Pinal Creek Basin near Globe, Arizona

By James G. Brown¹ and Judson W. Harvey²

Abstract

Acidic-mine drainage from copper mining in the Pinal Creek basin has contaminated the regional aquifer. Chemical reactions neutralize the contaminant plume as it moves downgradient. Neutralized contamination subsequently surfaces in a perennial reach of Pinal Creek and equilibrates with the atmosphere, causing pH to rise and manganese minerals to precipitate on the streambed. Ongoing research at the site is focused on ground-water hydrology and geochemistry, metal transport, and interactions between shallow ground water and streamflow.

Field and laboratory experiments will attempt to identify the reduction(s) that balance the oxidation of iron in the aquifer. Reactive-transport simulations of plume evolution and remediation will identify the important processes and reactions that produced the observed conditions in the plume. Measurements of gravity change and ground-water level change at project wells may provide refined estimates of aquifer specific yield for use in reactive-transport simulations. Estimates of ground-water ages by chlorofluorocarbon age-dating techniques may improve estimates of traveltimes and reaction rates of contaminants in ground water.

Mechanisms of trace-metal scavenging by manganese carbonates, manganese oxides, and iron oxides in the perennial stream are being investigated, and partitioning coefficients are being estimated to constrain hydrogeochemical modeling. A coupled aquifer-stream mass-balance approach has been used to constrain effective rates of solid-aqueous partitioning of manganese, iron, nickel, copper, and cobalt. Tracer experiments are being undertaken to distinguish reactions occurring in near-stream ground water from reactions in streamflow.

INTRODUCTION

The Pinal Creek basin, in central Arizona (fig. 1), has been an area of large-scale copper mining since the late 1880’s. Acidic drainage from mining and related activities has contaminated the regional alluvial aquifer. The U.S. Geological Survey began a study of the contamination with the following objectives: (1) Define the nature and extent of ground-water and surface-water contamination, (2) identify the reactions and processes occurring in the contaminant plume, and (3) develop and test the ability of geochemical and transport models to simulate observed conditions. The purpose of this paper is to provide an overview of the site and a summary of past and ongoing research at Pinal Creek.

GEOHYDROLOGY

The drainage area of Pinal Creek above Inspiration Dam is 516 km². About 170 km² of this area is underlain by a basin-fill conglomerate and a permeable stream alluvium, which together compose the regional aquifer. The aquifer is bounded laterally and at depth in most areas by relatively impermeable

Figure 1. Area of study.
rocks. The aquifer thins and becomes narrower from well site 500 (fig. 2) north to Inspiration Dam. This thinning and narrowing decreases the volume of water that can move and be stored in the subsurface, and sustains perennial flow into Pinal Creek. Streamflow in Pinal Creek is perennial in a 5-to 6 kilometer reach above Inspiration Dam.

Basin fill ranges from unsorted and unconsolidated boulders to well-stratified deposits of firmly cemented sand, silt, and gravel (Peterson, 1962, p. 41). Carbonate content of the basin fill is about 1.5 percent (Eychaner, 1989, p. 570). Horizontal hydraulic conductivity of basin fill is estimated to range from 0.1 to 0.2 m/day (C.G. Taylor, Magma Copper Corporation, written commun., 1987). Stream alluvium consists mainly of sand and gravel but includes stratified deposits of clay-sized material as much as 12 m thick locally. Horizontal hydraulic conductivity of alluvium between well sites 400 and 500 was estimated to be 260 m/d. Alluvium at well site 600 (fig. 2), through which neutralized, contaminated water has passed, contained from 0.3- to 0.7- percent carbonate material.

Ground-water levels in stream alluvium and adjacent basin fill respond rapidly to variations in recharge and pumping. Water levels declined steadily from 1986 to 1990 in response to less-than-average rainfall in the basin and increased pumping between Miami Wash and Pinal Creek for the purposes of remediation. The amount of ground-water decline generally decreased in a downstream direction. Ground-water levels rose as much as 16 m (fig. 3) adjacent to Miami Wash by February 1993 because of wetter than normal winters in 1991 and 1993.

NATURE AND EXTENT OF CONTAMINATION

Leakage of mine wastewater and process water from unlined impoundments into stream alluvium have contributed to a 15-kilometer-long acidic contaminant plume within the alluvium along Miami...
ground water discharges into the stream, gases dissolved in water reach equilibrium with the atmosphere. In the process, carbon dioxide (CO₂) degases, and pH rises to about 8 over a distance of about 5 km. Neutralized water from Pinal Creek at Inspiration Dam (Streamflow-gaging station 09498400) contained 560 mg/L dissolved calcium (Ca), 2,800 mg/L dissolved SO₄, and 39 mg/L dissolved manganese (Mn) in May 1992. Dissolved Fe and Cu concentrations were 0.01 and 0.006 μg/L (micrograms per liter), respectively. From 1984 to 1992, concentrations of Fe in water from well 51 decreased from 3,100 mg/L to 500 mg/L, and concentrations of SO₄ decreased from 10,000 mg/L to 2,700 mg/L (fig. 3). These decreases were caused by (1) removal of a significant source of contamination, (2) recharge from winter runoff in 1991-92, and (3) chemical reactions in the subsurface.

**RESEARCH IN PROGRESS**

Ongoing research falls within three general categories: ground-water geochemistry and transport, ground-water hydrology, and hydrochemical interactions between ground water and surface water. These broad categories provide the framework in which to discuss present research at the site.

**Ground-water geochemistry and transport**

Although the most important reactions in the aquifer are well understood, the redox reactions responsible for the observed decreases in dissolved Fe have not been adequately characterized. The results of geochemical modeling (Glynn and others, 1991) suggest that the dissolution of Mn oxide solids could be the principal reduction that balances Fe oxidation. Reactions involving Mn and Fe indicate that 2 mol of Fe should precipitate for each mole of Mn that dissolves, even though column experiments by Stollenwerk gave the ratio of 7 to 1 (Eychaner, 1991a). This ratio suggests that (1) Mn-oxide solids are reduced incongruently to form other Mn minerals, (2) other minerals or aqueous species might also be reduced, and (3) the atmosphere may be a significant source of O₂ to the plume. The incongruent dissolution of Mn-oxide solids and potential reduction of other minerals or aqueous species to balance the redox budget will be examined by a combination of laboratory work and geochemical modeling.

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**Figure 3.** Ground-water levels and concentrations of iron and sulfate adjacent to Miami Wash.
Figure 4. Distribution of pH in the aquifer in 1992. Line of section approximates the principal ground-water-flow line from Webster Lake to Inspiration Dam along the channels of Webster Gulch, Bloody Tanks Wash, Miami Wash, and Pinal Creek.

Table 1. Chemical analyses of contaminated water in Pinal Creek basin

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<th>Date sampled</th>
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<th>Well 451</th>
<th>Well 503</th>
<th>Station 09498400</th>
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<tr>
<td></td>
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<td>Temperature (°C)</td>
<td>Specific conductance (µS/cm)</td>
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<td>7.8</td>
<td>20.0</td>
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<td>560</td>
</tr>
</tbody>
</table>

Glynn and others (1991) simulated chemical reactions and transport in the subsurface with the model PHREEQM and found a tendency for the predicted pH to be higher than pH measured in the field. Exsolution of CO₂ will be measured at the leading edge of the acidic part of the plume to determine the contribution of this process to the pH and redox balance and ultimately to contaminant transport. Preliminary gas measurements of CO₂ in the unsaturated-zone at site 500 indicate a diffusion-induced fractionation of 4.4 per mil for carbon ¹³C over a distance of 2.38 m between neutralized water at the water table and the land surface—the fractionation expected for a steady-state upward flux of CO₂ (Glynn and Busenberg, 1996). Pierre D. Glynn, (U.S. Geological Survey, National Research Program, Reston, Virginia), plans to measure exsolution and estimate the flux of CO₂ at or near the leading edge of the acidic part of the plume.
The testing, verification, and application of coupled geochemical-transport models also will help answer some of the remaining questions about subsurface-contaminant transport. General testing of reactive-transport models and the use of sensitivity analyses to define the most important reactions will be continued by Glynn, in cooperation with Peter Engesgaard (Technical University, Denmark) and Kenneth L. Kipp (U.S. Geological Survey, Denver, Colorado). James G. Brown, (U.S. Geological Survey, Tucson, Arizona), R.L. Bassett (University of Arizona, Tucson, Arizona), and Glynn plan to use a sensitivity-analysis type of approach to identify and determine the relative importance of chemical reactions, dilution, and transport that may control the remediation and chemical recovery of the regional aquifer. Brown, Bassett, and Glynn also plan to simulate transient, reactive transport in two dimensions, accounting for redox, adsorption, dissolution-precipitation, complexation, and hydrolysis.

Ground-Water Hydrology

Adequate simulation of reactive-solute transport through the subsurface depends on the accuracy of estimating recharge to the aquifer and subsurface-hydrological transport. D.R. Pool (U.S. Geological Survey, written commun., 1993) estimated changes in storage and specific yield in the alluvium on the basis of observed changes in ground-water level and gravity, and plans similar measurements between Miami Wash and Pinal Creek. Average values of specific yield of sediments that were saturated by water-level rises are from 0.16 to 0.21. Larger specific-yield values were associated with sediments containing large percentages of sand and gravel. Small specific yields were associated with sediments finer than sand.

Pierre Glynn and Eurybiades Busenberg (U.S. Geological Survey, National Research Program, Reston, Virginia) measured chlorofluorocarbon (CFC) concentrations in ground water to estimate ground-water ages in the basin. Preliminary results using CFC-11 for age-dating indicate that ground water from a depth of about 18 to 27 m in alluvium upgradient from contamination sources was recharged in 1979 (Glynn and Busenberg, 1996). Planned additional measurements of CFC's may indicate if an assumption of steady-state flow for reactive-transport modeling is valid. Travel-time information derived from these measurements, combined with the results from geochemical modeling, may provide estimates of chemical reaction-rates at the site.

Metal Transport in Shallow Ground Water and Streamflow

The acidic ground-water plume has moved downgradient at a rate of about 0.25 km/yr over the past several decades (Eychaner, 1991a). Higher-than-normal rainfall in 1991-93 increased ground-water levels by as much as 15 m and moved the headwaters of perennial flow upvalley. In early 1993, acidic-contaminated ground water in Miami Wash rose temporarily to the ground surface and discharged directly to streamflow. The headwater of perennial streamflow has since reestablished itself 1 km upstream from the location shown in figures 1 and 3. Increased hydraulic gradients and shortened ground-water flow paths may cause the acidic core of the plume to reach perennial surface water sooner than expected, depending on the transport of uncontaminated recharge water and the degree of mixing of uncontaminated recharge water with the contaminated water in the plume. Chemical mass-balance models and ground-water-flow modeling, where needed, will be used by Harvey and others to investigate the consequences of enhanced interaction between ground water and surface water on mass-flow rates of contaminants out of the basin.

Neutralized contaminated ground water with large Mn concentrations (table 1, well 503) is being discharged to the perennial reach of Pinal Creek. High pCO₂ and low pO₂ of contaminated ground water is modulated by gas exchange with the atmosphere after ground water discharges to the stream. Resulting increases in pH and pe favor Mn oxidation (Eychaner, 1991b). Concentrations of colloidal Fe and Mn presently in streamflow are low compared to total concentrations in solution (Harvey and Fuller, 1996). The absence of high Mn colloid concentrations suggests that Mn is partitioned to solid phases mostly on surfaces of streamed solids. Colloidal transport of Fe, Mn, and other trace metals appears in general to be only a minor mechanism of metal transport during baseflow in Pinal Creek. The role of Fe colloids in trace-metal transport will likely increase if the acidic core of the contaminated plume reaches Pinal Creek.

The character and chemical composition of manganese precipitates on the streamed at Pinal Creek vary considerably (Lind and Hem, 1993). J.D. Hem and C.J. Lind (U.S. Geological Survey, Menlo Park, California) are continuing their studies of chemical controls on manganese mineral formation at the site. Mn carbonate precipitation on streamed
sediments appears to be favored initially in upstream reaches; Mn oxide precipitation becomes more important as pH and availability of dissolved oxygen both increase farther downstream (Hem and Lind, 1996). Fe and Mn oxides and carbonate minerals on the streambed scavenge other dissolved trace metals, including nickel (Ni), copper (Cu), and cobalt (Co), from surface flow. Trace metals have an decreasing affinity for Fe oxides, Mn oxides, and carbonate minerals, in decreasing order (Lind and Anderson, 1992). The greater abundance of Mn solid phases compared to Fe solid phases suggests that trace metal partitioning may be controlled by reactions with Mn phases. Chris Fuller (U.S. Geological Survey, Menlo Park, California) is investigating the relative roles of trace-metal coprecipitation and adsorption on Mn phases on the streambed as mechanisms for attenuation of dissolved Ni, Cu, and Co in streamflow (Fuller, 1996). The goals are to determine dominant chemical mechanisms of trace-metal partitioning to solid phases and to estimate partitioning coefficients for improved hydrochemical modeling.

Harvey and others (1996) showed that significant partitioning of Mn and Fe occurs between solid and aqueous phases in shallow ground water before ground water is discharged into Pinal Creek. A gain in Fe and loss of Mn from solution occurs in ground water that discharges laterally through the stream-channel banks at Pinal Creek; in contrast, ground water that discharges vertically through the creek bottom is unaltered by chemical reaction. A coupled mass balance for 500 m of stream and the surrounding aquifer in November 1992 demonstrated the importance of reactions in shallow ground water on downstream water chemistry in Pinal Creek.

Water exchange between streamflow and streamwater-filled flow paths in streambed sediments was investigated at Pinal Creek by a bromide-tracer experiment. Exchange between streamflow and ground water affects the contact area and contact times of streamflow with streambed solids. Rates of Mn oxidation and trace-metal sorption on streambed surfaces, therefore, may be sensitive to surface water-ground water hydrological exchange. Preliminary data are being used by Harvey, Fuller, and Conklin (University of Arizona, Tucson, Arizona) to design future experiments at Pinal Creek. Aspects of identifying the structure of improved hydrochemical models for Pinal Creek and of estimating model parameters and associated uncertainties are outlined in Wagner and Harvey (1996).

**SUMMARY**

Acidic drainage from copper mining has contaminated the regional alluvial aquifer in the Pinal Creek basin. The acidic contamination is neutralized along the flowpath by reactions with aquifer materials and native ground water. Neutralized water discharges in a perennial reach of Pinal Creek; as the water equilibrates with the atmosphere, pH increases and Mn minerals precipitate on the streambed.

Ongoing research at the site is focused on ground-water geochemistry, hydrology, and solute transport and interactions between ground water and perennial streamflow. Field and laboratory experiments will attempt to identify the reduction(s) that balance the oxidation of Fe in the aquifer. Two-dimensional reactive-transport simulations of plume evolution and remediation will identify the important processes and reactions that produced the observed conditions in the plume.

Measurements of changes in gravity and levels of ground water at project wells may provide refined estimates of aquifer specific yield for use in reactive-transport simulations. Estimates of ground-water ages obtained by CFC age-dating techniques may provide improved estimates of ground-water travel times and, when combined with results from geochemical modeling, provide estimates of geochemical-reaction rates at the site.

Field, laboratory, and modeling studies of contaminant transport are being conducted to improve understanding of the controls on metal transport in near-stream ground water and in streamflow. Previous work showed that Mn precipitates are variable and complex, and that precipitation is generally controlled by CO₂ outgassing and reaeration, which affects pH and the solubility of Mn solids. Mechanisms of trace-metal scavenging by Mn carbonates, Mn oxides, and Fe oxides are being investigated, and partitioning coefficients are being estimated to improve hydrogeochemical modeling. Tracer experimentation and a coupled aquifer-stream mass-balance approach are being used to determine transport components and to constrain net effective rates of solid-aqueous partitioning of Mn, Fe, Ni, Cu and Co in the system.
REFERENCES CITED


Dissolved Gas and Chlorofluorocarbon Content of Ground Waters in the Pinal Creek Basin, Arizona

By Pierre D. Glynn¹ and Eurybiades Busenberg¹

Abstract

Dissolved nitrogen and dissolved argon concentrations in ground waters at the Pinal Creek toxic waste site were used to calculate recharge temperatures and excess air trapped during recharge. The average recharge temperature was about 12±2 °C -- 6 to 7 °C colder than the average ground water temperatures. Excess-air concentrations were up to 11 milliliters per liter, indicating very rapid recharge probably during flooding events in the winter and early spring. This hypothesis is supported by local precipitation and air temperature records as well as by the 10 °C temperature recorded in Final Creek during a large recharge event in February 1993. Nitrogen production by denitrification is not thought to be significant. Dissolved oxygen concentrations are high in all uncontaminated ground waters, a finding consistent with low organic carbon contents in the aquifer. High carbon dioxide partial pressures (pCO₂) were measured in the contaminated ground waters, particularly in the neutralized contaminated ground waters. Dissolution of carbonate minerals by acid-contaminated ground water is thought to be responsible for the high pCO₂ values. Chlorofluorocarbon-12 (CFC-12) and chlorofluorocarbon-11 (CFC-11) concentrations decrease with depth and distance downgradient in the metal- and acid-contaminated ground waters. CFC-12 concentrations are abnormally high and are thought to result from historically higher-than-normal atmospheric concentrations rather than from point-source ground-water contamination. Ground-water ages calculated from CFC-11 concentrations are reasonable -- 3 to 15 years for acid-contaminated ground waters and 20 to 30 years for neutralized contaminated ground waters. Deep uncontaminated ground waters have no significant CFC-11 or CFC-12 concentrations, and are believed to more than 50 years old. The CFC-11 recharge dates are consistent with available tritium, deuterium, oxygen-18, and dissolved-gas data.

INTRODUCTION

This paper presents preliminary data gathered during a field trip to the Pinal Creek toxic waste site in late November 1991. The primary objective of the trip was to determine the possibility of obtaining reproducible measurements of chlorofluorocarbon (CFC) concentrations, at the picogram-per-kilogram level, in the metal- and acid-contaminated ground waters of the Pinal Creek basin (fig. 1). A secondary objective was to determine whether the measured concentrations could be used to age date the ground waters and, therefore, refine our understanding of the flow system. We believe that this paper presents the first measurement of CFC concentrations in metal- and acid-contaminated ground waters.

Dissolved-gas samples also were collected and analyzed for nitrogen (N₂), argon (Ar), oxygen (O₂), carbon dioxide (CO₂) and methane (CH₄). N₂ and Ar measurements were needed to determine recharge temperatures used to calculate ground-water recharge dates from CFC concentrations. The dissolved-gas analyses also provide information on reactions occurring in ground water. This paper reports results of our dissolved-gas study and the implications of these results on knowledge of the inorganic processes occurring in the ground water.

Figure 1. Area of study.
We are grateful to James Brown, Steve Longsworth, and Dorrie Gellenbeck for their invaluable help in collecting the field data presented in this paper. We also thank Rosalynd Williams, Julian Wayland and Ray Van Hoven, for their laboratory analyses of our samples.

SAMPLING PROCEDURE

Dissolved-gas sampling procedures are described in Hobba and others (1977) and Pearson and others (1978). The dissolved-gas samples were collected after three well-casing volumes had been purged, after temperature, pH, and dissolved oxygen concentrations had stabilized, and after samples had been collected for standard chemical analysis. The wells were usually pumped at 10 gallons per minute (38 liters per minute) with a Grundfoss pump.

After removing the pump and its associated polyvinylchloride sampling pipe, a Keck pump with copper tubing was lowered into the wells. After a 10 to 30 minute purge, six water samples per well were collected at 5 to 6 minute intervals for CFC analysis. The samples were sealed in glass ampules following the procedure described by Busenberg and Plummer (1992).

DISSOLVED-GAS CONCENTRATIONS IN PINAL CREEK GROUND WATERS

The dissolved-gas samples were analyzed by gas chromatograph in the laboratory for dissolved N₂, Ar, O₂, CO₂, and CH₄. CH₄ concentrations were below the detection limit (0.1 mg/L) in all samples.

The use of CFC concentrations to assign ground-water recharge dates requires knowledge of the temperature of recharge as well as the amount of excess air entrapped during the recharge process. Measurements of dissolved nitrogen and dissolved argon concentrations provide a convenient method for estimating these two parameters (Busenberg and Plummer, 1991; Busenberg and others, 1993).

Some of the factors affecting dissolved N₂ and Ar concentrations measured in ground water are (1) the composition of the gas phase at the time of water-gas equilibration, (2) the relative humidity of the gas phase, (3) the temperature at the time of equilibration, (4) the barometric pressure at the time of equilibration, (5) the amount of excess air (or soil gas) entrained during the recharge process, (6) the ionic strength of the water, (7) the amount of N₂ produced by denitrification reactions in the ground water, (8) gas loss by exsolution during sampling, (9) gas-exchange processes near the water table after recharge, (10) diffusion and dispersion of dissolved gases in ground water, and (11) mixing of waters with distinct dissolved-gas contents during sampling. The assumptions made in calculating recharge temperatures and excess-air concentrations from dissolved N₂ and Ar concentrations are that factors 6 through 11 can be neglected. We also assume that the gas phase at the time of equilibration has average air composition, and that the barometric pressure at the time of equilibration can be calculated from an estimate of the applicable recharge elevation and a standard function relating atmospheric pressure to altitude. N₂ and Ar solubilities as a function of temperature were calculated by use of equations and constants given in Wilhelm and others (1977).

Dissolved N₂ and Ar concentrations are shown in figure 2A. Table 1 provides a summary of the well characteristics associated with the well numbers given in the graph. Recharge temperatures and excess-air concentrations calculated from the N₂ and Ar data are shown in figure 2B. Calculations were made assuming a minimum recharge elevation of 900 m and a maximum elevation of 1374 m. The N₂ and Ar results for well 52 are suspect because they lie outside the generally linear trend of N₂ and Ar concentrations; the Ar concentration is disproportionately high compared to the N₂ concentration, and the calculated recharge temperature is unrealistically low.

Recharge elevation affects calculated recharge temperature but does not significantly affect calculated excess-air concentration, as shown in figure 2B. Changing recharge elevation results in a difference of 0.12 mL/L in excess-air concentration. In comparison, calculated temperatures for any given water sample vary by about 2 °C, depending on the recharge elevation used. Measurement uncertainties in the N₂ and Ar analyses also correspond to a 2 °C uncertainty in the calculated recharge temperatures. Considering these uncertainties, the fact that all the wells sampled for CFC's were not sampled for dissolved gases, and the lack of duplicate samples, we decided to use an average recharge temperature of 12 °C to calculate recharge dates from CFC concentrations. This temperature is markedly lower than the average ground-water temperature of 18 to 19 °C, which indicates that recharge must occur predominantly during winter and early spring. This hypothesis is supported by the 10 °C temperature of a water sample from Pinal Creek.
Table 1. Characteristics of ground water wells sampled in the Pinal Creek Basin in November 1991.

<table>
<thead>
<tr>
<th>Well number</th>
<th>Screen depth</th>
<th>Screen length</th>
<th>Aquifer material</th>
<th>Water type</th>
</tr>
</thead>
<tbody>
<tr>
<td>010</td>
<td>27.1</td>
<td>9.1</td>
<td>bf</td>
<td>u</td>
</tr>
<tr>
<td>2</td>
<td>19.8</td>
<td>.9</td>
<td>al</td>
<td>a</td>
</tr>
<tr>
<td>53</td>
<td>27.8</td>
<td>.9</td>
<td>bf</td>
<td>a</td>
</tr>
<tr>
<td>51</td>
<td>33.4</td>
<td>.9</td>
<td>al</td>
<td>a</td>
</tr>
<tr>
<td>102</td>
<td>25.2</td>
<td>.9</td>
<td>al</td>
<td>a</td>
</tr>
<tr>
<td>103</td>
<td>25.3</td>
<td>.9</td>
<td>al</td>
<td>a</td>
</tr>
<tr>
<td>101</td>
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<td>a</td>
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<td>105</td>
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<td>n</td>
</tr>
<tr>
<td>304</td>
<td>30.3</td>
<td>.9</td>
<td>al</td>
<td>a</td>
</tr>
<tr>
<td>302</td>
<td>35.8</td>
<td>.9</td>
<td>al</td>
<td>a</td>
</tr>
<tr>
<td>402</td>
<td>20.9</td>
<td>.9</td>
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<td>a</td>
</tr>
<tr>
<td>401</td>
<td>34.2</td>
<td>.9</td>
<td>bf</td>
<td>a</td>
</tr>
<tr>
<td>404</td>
<td>55.3</td>
<td>.9</td>
<td>bf</td>
<td>u</td>
</tr>
<tr>
<td>452</td>
<td>8.2</td>
<td>3.0</td>
<td>a</td>
<td>n</td>
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<td>451</td>
<td>24.4</td>
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<td>bf</td>
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</tr>
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<td>506</td>
<td>6.7</td>
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<td>al</td>
<td>n</td>
</tr>
<tr>
<td>501</td>
<td>17.0</td>
<td>.9</td>
<td>al</td>
<td>n</td>
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<tr>
<td>503</td>
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<td>.7</td>
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<td>n</td>
</tr>
<tr>
<td>502</td>
<td>38.0</td>
<td>.9</td>
<td>bf</td>
<td>n-u</td>
</tr>
<tr>
<td>504</td>
<td>69.2</td>
<td>1.0</td>
<td>bf</td>
<td>u</td>
</tr>
<tr>
<td>701</td>
<td>4.7</td>
<td>.9</td>
<td>al</td>
<td>n</td>
</tr>
<tr>
<td>702</td>
<td>7.3</td>
<td>.9</td>
<td>al</td>
<td>n</td>
</tr>
</tbody>
</table>

The calculated excess-air concentrations are relatively high, compared to concentrations found for shallow ground waters in the Delmarva peninsula (generally less than 3 mL/L; Dunkle and others, U.S. Geological Survey, written commun., 1993), but are consistent with results from other semiarid areas, where rapid recharge occurs during intense precipitation and flooding events. For example, ground waters in the western Kalahari in South Africa contain 4 to 16 mL/L of excess air (Heaton and others, 1983).

Ground waters from the deepest wells sampled (404, 504 and 105) contain the highest calculated excess-air concentrations -- up to 11 mL/L -- and, together with water from well 52, have the highest N₂ and Ar concentrations. Water from wells 404 and 504 is uncontaminated, whereas water from well 105 is neutralized contaminated water. The dissolved oxygen data, shown in figure 2C, show that ground water at all three uncontaminated wells (010, 504, 404) have high dissolved O₂ concentrations and the lowest specific conductance of all ground waters sampled. Water from well 105 has a significant O₂ concentration that may represent a mixture of background uncontaminated

Figure 2 (A). Dissolved argon and nitrogen concentrations measured in Pinal Creek ground waters. The excess-air vector and the line representing equilibrium with air as a function of temperature and elevation are given for reference.

(unpublished data in the files of the U.S. Geological Survey, Tucson district office). The sample was collected during a large recharge event (at a flow of 1000 cubic feet per second in Pinal Creek) at Inspiration Dam in February 1993 (fig. 1).

Our calculated recharge temperatures are supported by monthly precipitation and air-temperature records for Miami, Arizona, provided by the National Weather Service. The records indicate that, on average, 21 cm of precipitation (out of a yearly total of 50 cm) fall during the months of December through March and that the mean air temperature during that period is 8.5 °C. The other wet period of the year occurs in July and August and contributes on average 14 cm of precipitation. The average air temperature during July and August is 27.8 °C, and evaporation is undoubtedly significant, although flash floods are common during that period.
water and neutralized contaminated water. The calculated equilibrium partial pressures of O$_2$ and N$_2$ at the measured ground-water temperatures (generally 18-19 °C, 15.5 °C for well 010) are shown in figure 2D.

The atmospheric partial pressures of N$_2$ and O$_2$ are 0.69 and 0.19 atm at an elevation of 950 m (mean atmospheric pressure is 0.893 atm), and are even lower at higher elevations. Consequently, N$_2$ partial pressures (pN$_2$) in all sampled ground waters exceeded mean atmospheric pressure, and N$_2$ was likely to degas if the ground waters were brought in contact with the atmosphere. Degassing of these ground waters could also possibly occur in situ at depths of up to 2 m below the water table (Glynn and Busenberg, 1996). Waters from wells 404, 504 and 105 had the highest pN$_2$ values (up to 1.3 atm). Waters from these wells also have high dissolved Ar concentrations in proportion to dissolved N$_2$ concentrations.

The calculated equilibrium partial pressures of CO$_2$ as a function of pH are shown in figure 2E. Apart from the uncontaminated ground waters at wells 404, 504 and 010, and the contaminated but neutralized water at well 702, all other ground water samples also contained high pCO$_2$ values well in excess of the atmospheric partial pressure (0.031 atm at an elevation of 950 m), as shown in figure 2E. Water from these wells also had pH values less than 6, with the exception of the neutralized water in well 105, which had a pH of 6.4. At pH values less than 6.3, dissolved CO$_2$ is the dominant form of dissolved inorganic carbon, and acidification of an uncontaminated ground water will
by itself increase the equilibrium $pCO_2$ of the water. As the acid-contaminated ground waters (with already elevated $pCO_2$ values) become progressively neutralized (pH increases), $pCO_2$ values increase further as a result of the dissolution of carbonate minerals in the aquifer materials, as shown in figure 2E. The high $pCO_2$ values are thought to be responsible for a flux of approximately $9 \times 10^{-3}$ (mol/m²)/d of CO₂ through the unsaturated zone at well sites 450 and 500 (Glynn and Busenberg, 1996).

**CHLOROFUOROCARBON CONTENTS AND RECHARGE DATES OF PINAL CREEK GROUND WATERS**

CFC concentrations can be used to date ground waters if the concentrations measured reflect the equilibrium that was present between the atmospheric CFC concentrations and the ground water at the time of recharge. CFC-11 and CFC-12 concentrations have, since the 1940's and until recently, increased exponentially in the atmosphere. Therefore, recent ground waters should have higher CFC concentrations than older waters. CFC concentrations can not be used to age-date ground waters if (1) contamination from nonatmospheric sources has occurred, (2) local atmospheric concentrations differ significantly from average continental concentrations, (3) significant CFC degradation occurs in the ground-water environment (degradation occurs only in highly reducing environment and affects CFC-11 more strongly than CFC-12) and, (4) significant sorption of CFC's occurs (of concern in the presence of organic-rich aquifer materials and affects CFC-11 concentrations more strongly than CFC-12 concentrations). Busenberg and Plummer

![Figure 2 (D). Equilibrium partial pressures of oxygen and nitrogen calculated from dissolved-gas concentrations for Pinal Creek ground waters at ground-water temperatures measured in the field.](image)

![Figure 2 (E). The relation between measured pH and partial pressures of carbon dioxide calculated for Pinal Creek ground waters (at field temperatures).](image)
Acid-contaminated ground waters at the Pinal Creek site have low dissolved organic carbon concentrations (4.2 mg/L), but these concentrations were nevertheless found to be up to eight times greater than the concentrations in background uncontaminated waters in 1988 and 1989 (Reese and Bassett, 1990). The presence of polycyclic aromatic hydrocarbons, found in the more acidic ground waters at the Pinal Creek site, indicated an anthropogenic source for the increase in dissolved organic carbon (Wallin and others, 1991), and raised the possibility of localized anthropogenic contamination of CFC's; such contamination would have precluded the use of CFC concentrations to assign ground-water recharge dates. Fortunately, aquifer materials at the site contain low concentrations of organic carbon, and the ground waters are not strongly reducing. This knowledge minimized concerns about possible CFC biodegradation and sorption.

The concentrations of CFC-12 and CFC-11 are shown in figures 3 and 4. The CFC-12 concentrations commonly exceed concentrations expected for water at equilibrium with 1991 average continental atmospheric concentrations and, with a few exceptions, cannot be used to date the ground waters. Nevertheless, CFC-12 concentrations seem to decrease both as a function of depth and distance downgradient, as shown in figure 3. The highest CFC-12 concentrations near the water table are about 315 pg/kg (wells 52, 304, 402), with the exception of water in well 103 (648 pg/kg). The concentrations in waters from wells 52, 304 and 402 are close to the concentration expected for a background water recharged in late

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**Figure 3.** Hydrogeologic section showing chlorofluorocarbon-11 concentrations in Pinal Creek ground waters.
Figure 4. Hydrogeologic section showing chlorofluorocarbon-12 concentrations in Pinal Creek ground waters.

1991 (approximately 270 pg/kg). Therefore, the possibility exists that air in the Pinal Creek valley may have had higher than normal CFC-12 concentrations and may be the cause for the high CFC-12 concentrations observed in the ground waters.

CFC-11 concentrations show the same overall trends as the CFC-12 concentrations. CFC-11 concentrations generally decrease with depth and distance downgradient, with the exception of water from well 702 (well site 700), which has a CFC-11 concentration of 565 pg/kg, typical of waters recharged in 1987-88 (fig. 4).

Preliminary recharge dates calculated from CFC-11 data (and a few CFC-12 data) are shown in table 2 and figure 5. The dates of recharge were calculated using a recharge temperature of 12 °C and a recharge altitude of 1372 m. As additional dissolved-gas data become available and an understanding of the ground-water-flow system improves, the recharge temperature and recharge elevations used in the age-dating calculations will be refined. Excess-air concentrations of less than 20 mL/L do not significantly affect calculated CFC-based recharge dates (Busenberg and others, 1993) and, therefore, excess-air concentrations are not taken into account in our calculations. It is important to remember that, although individual recharge dates are assigned to specific water samples, the water samples themselves will generally represent a mixture of waters of different ages.

Table 2 shows the good agreement between the calculated CFC-11- and CFC-12-based recharge dates for waters from well 010, illustrating the accuracy that can be expected for CFC-based recharge dates in recent uncontaminated ground waters (well 010 was the only well sampled that had recent uncontaminated ground water). The results show that younger water
was being pumped from the well as sampling time progressed (samples were collected approximately 6 minutes apart). The CFC-12-based recharge dates are a little more recent than the CFC-11-based recharge dates, but the difference is probably not significant. Unlike the other wells sampled, well 010 is located south of the mining and refining operation areas, south of the towns of Globe and Miami. Precipitation that recharged ground waters sampled at well 010 does not appear to have been exposed to the higher-than-normal CFC-12 atmospheric concentrations that may have prevailed at lower elevations on the other side of Miami.

**Table 2.** Chlorofluorocarbon recharge dates for recent uncontaminated ground waters in the Pinal Creek Basin from well 010

<table>
<thead>
<tr>
<th>Sample number</th>
<th>CFC-11 (pg/kg)</th>
<th>CFC-12 (pg/kg)</th>
<th>CFC-11 date</th>
<th>CFC-12 date</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>202.6</td>
<td>88.6</td>
<td>1972.5</td>
<td>1972.0</td>
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<tr>
<td>2</td>
<td>315.8</td>
<td>146.4</td>
<td>1976.5</td>
<td>1978.0</td>
</tr>
<tr>
<td>3</td>
<td>397.5</td>
<td>168.9</td>
<td>1980.5</td>
<td>1981.0</td>
</tr>
<tr>
<td>4</td>
<td>372.9</td>
<td>176.3</td>
<td>1979.0</td>
<td>1981.5</td>
</tr>
<tr>
<td>5</td>
<td>370.6</td>
<td>174.2</td>
<td>1979.0</td>
<td>1981.5</td>
</tr>
</tbody>
</table>

Ground water from the deepest uncontaminated wells, 404 and 404, contains no significant CFC concentrations and is, therefore, thought to have been recharged before 1940. Ground water from the next deepest well sampled, well 105, has a recharge date of 1962. Tritium analyses of ground waters sampled in June 1988 and May 1989 (Brown, 1990) agree with these results. Water from well 404 contained a tritium concentration of 0.5 pCi/L (close to the detection limit of 0.3 pCi/L) and water from well 404 did not contain detectable tritium. This would indicate a pre-1953 recharge date for these waters. Water from well 105, however, has a tritium concentration of 47 pCi/L, the second highest value measured in Pinal Creek ground waters, indicating a post-1953 recharge date consistent with the CFC-based recharge date of 1962. (The highest measured tritium concentration was 86 pCi/L in ground water from well 301; unfortunately, this well was not sampled in the November 1991 field trip).

Water from wells 504 and 404 is also depleted in oxygen-18 by 2 to 3 per mil and in deuterium by 20 per mil relative to the contaminated ground waters (Longsworth and Taylor, 1992). This depletion indicates that recharge of ground waters from wells 504 and 404 occurred at higher elevations and probably at colder temperatures than the recharge of contaminated shallow ground waters. Waters from wells 504 and 404 are presently thought to have been recharged in the mountains east of the valley, whereas shallow contaminated ground waters originate, at least in part, from Webster Lake (J.G. Brown, U.S. Geological Survey, written commun., 1993).

CFC-based recharge dates for the acidic ground waters at well sites 050, 100, 300, 400, and 450 range from 1976 to 1988, suggesting travel times of 3 to 15 years. The CFC-11-based recharge dates for the contaminated ground waters are consistent with the date of formation of Webster lake in 1940. Tritium concentrations that generally range from 22 pCi/L to 86 pCi/L in all contaminated ground waters (except for ground water at well 502, see below) at the Pinal Creek study site (Brown, 1990) also suggest post-1953 recharge dates.

Results from particle tracking simulations (Brown, 1991) show shorter travel times than those calculated from CFC-based recharge dates. According to the particle tracking simulations, the maximum estimated travel time between Webster lake and Inspiration Dam is 15 years. The ground-water-flow model on which Brown's (1991) particle-tracking analysis was based is currently considered inadequate in its simulation of flow in the basin fill. Nevertheless, travel time estimates derived from the ground-water-flow model for the alluvium are reasonable. An average travel time between Webster lake and Inspiration Dam of 8 years (4.2 minimum, 13 years maximum) can be calculated from Darcy's law (J.G. Brown, U.S. Geological Survey, written commun., 1993). The average gradient is 0.008 m/m (calculated from water table levels). Horizontal hydraulic conductivities range from 150 to 260 m/d (determined from aquifer tests) and porosity ranges from 0.14 to 0.26 (from measured specific yields and gravity-change measurements). The distance between Webster lake and Inspiration Dam is 23 km. Using similar calculations, J.G. Brown (U.S. Geological Survey, written commun., 1993) estimates minimum and maximum travel times of 0.9 years and 3 years in the alluvium between Webster lake and well site 50. In comparison, ground waters sampled from the shallowest well at sit 50, well 52, had an average CFC-based recharge date of 1986, for a CFC-based age of 5 ± 2 years.
Recharge dates for neutralized contaminated ground waters at well site 500 range from 1969 to 1972. Ground water from well 502 has a chemical composition indicative of a mixture of contaminated neutralized ground water and old uncontaminated ground water; the CFC-11-based recharge date is 1964. The tritium concentration in a water sample from well 502 in January 1989, however, was less than 5.7 pCi/L (Brown, 1990), indicating either an older recharge date, certainly pre-1964, or a disproportionately large amount of old water in the January 1989 water sample.

The older recharge dates of the ground waters from well site 500 -- compared to upgradient shallow ground waters -- probably result from convergent flow caused by vertical and lateral constriction of the alluvium and basin fill at the northern downgradient end of the Pinal Creek valley (figs. 1 and 3). The convergence may have increased the mixing of old waters with more recent waters during sampling. For the same reason, neutralized contaminated ground waters from wells 701 and 702, downgradient from site 500, may have older CFC-based recharge dates (1960 - 1967) than those determined for ground waters from similar depths at site 500.

The CFC-11-based recharge dates of contaminated ground waters at the Pinal Creek site presented in this paper await confirmation from additional field studies and ground-water age-dating.
Even if confirmed, CFC-based recharge dates should always be used with caution. First, groundwater samples commonly represent a mixture of waters of differing ages, in which case the CFC-based age should be considered more an average, rather than a specific residence time. Secondly, unlike most other solutes in the contaminated ground waters of the Pinal Creek basin, CFC-11 and CFC-12 are presumed to be inert tracers. Their concentrations in ground water are not thought to be modified by chemical reactions. As a result, a CFC-based age can, at best, be considered only a minimum age of reactive contaminant solutes, because the subsurface transport of reactive solutes will generally be retarded with respect to the flow of the water and the transport of its inert solutes (Glynn and others, 1991).

**SUMMARY**

Preliminary findings of our study are—

1. Recharge temperatures calculated on the basis of dissolved N$_2$ and Ar concentrations are on average 6 °C cooler than the average ground-water temperature of 18 °C. Recharge temperatures calculated for ground waters from the deeper wells (404, 504 and 51, especially), screened in the basin fill, are lower than those calculated for ground waters from shallow wells screened in the alluvium.

2. Excess-air concentrations calculated from dissolved N$_2$ and Ar concentrations range from 1 to 11 mL/L of water. Ground waters from the deepest wells sampled (wells 404, 105, and 504) had the highest excess-air concentrations.

3. The high excess-air concentrations and low recharge temperatures calculated (compared to the mean annual air temperature) suggest that significant ground-water recharge occurs as a result of flooding in the winter and in the early spring. The low calculated recharge temperatures are supported by the 10 °C temperature of Pinal Creek measured during a large recharge event in February 1993, and also by available precipitation and air-temperature records for the area.

4. N$_2$ equilibrium partial pressures, calculated at field ground-water temperatures, always exceeded atmospheric partial pressures by as much as a factor of 2 in the case of water from well 404. Excess air entrapped during recharge, rather than N$_2$ production by denitrification is considered to be the cause.

5. Dissolved O$_2$ was present in all uncontaminated ground waters, including deep ground waters from wells 404 and 504. This finding is consistent with the low concentration of organic carbon in the alluvium and basin-fill aquifers, and with the low dissolved organic carbon concentration in the ground waters.

6. Dissolution of carbonate minerals by acid-contaminated ground waters is thought to be responsible for the high CO$_2$ equilibrium partial pressures (as high as 0.15 atm) calculated for the acid-contaminated and neutralized contaminated ground waters.

7. CFC-12 and CFC-11 concentrations in ground water decrease as a function of depth and distance downgradient at well sites 50, 100, 300, 400, 450, 500 and 700. Most CFC-12 concentrations exceed 270 pg/kg of water, the CFC-12 concentration expected for equilibrium with late 1991 continental air. Historically higher-than-normal atmospheric CFC-12 concentrations in the Pinal Creek valley are thought to be responsible, as opposed to direct point-source contamination of the ground waters.

8. Recharge dates based on CFC-11 and CFC-12 concentrations in uncontaminated ground waters at well 010 are within 2 years of each other. Unlike the other wells sampled, well 010 is located south of the mining and refining-operation areas, south of the towns of Globe and Miami. Precipitation that recharged ground waters sampled at well 010 does not appear to have been exposed to higher-than-normal CFC-12 atmospheric concentrations.

9. Recharge dates based on CFC-11 concentrations in contaminated waters from well sites 50, 100, 300, 400, 500 and 700 are reasonable. Postulated ground water ages range from 3 to 15 years except for ground waters from site 500 which are 20 years old. The older age of ground waters from site 500 and the even older age of ground waters from site 700 (determined from CFC-12 concentrations) are thought to result from the upward flow of old ground waters from the basin fill.

10. Deep uncontaminated ground waters from wells 404 and 504 did not contain any significant CFC-11 or CFC-12 concentrations. Recharge dates for these ground waters must, therefore, predate 1940. This finding is consistent with available tritium, deuterium, oxygen-18 and dissolved-gas data. The latter data suggest that ground waters at wells 404 and 504 were recharged before 1953, at a higher elevation and at colder temperature than that of sampled contaminated ground waters. The contaminated ground waters...
are thought to have been recharged, at least in part, from Webster lake.

CFC-based ground-water age can only at best give minimum ages for most of the contaminant solutes in ground waters of the Pinal Creek basin, because the subsurface transport of those solutes will generally be retarded by chemical reactions relative to the movement of the water and to the transport of inert solutes, such as CFC-11 and CFC-12.

REFERENCES


Abstract

Unsaturated-zone gases were sampled in November 1991 at two sites in the Pinal Creek basin, above the acidic to partially neutralized ground-water-contaminant plume. The gases were analyzed for carbon dioxide (CO$_2$), oxygen (O$_2$), nitrogen and argon. The isotopic composition of the CO$_2$ gas also was measured. Results show a linear CO$_2$ and O$_2$ gradient. An oxygen flux towards the water table of approximately 1.1x10$^{-2}$ (mol/m$^2$/d) is estimated. This oxygen flux is probably caused by the reaction of dissolved oxygen with reduced manganese and iron in the ground water. A steady-state flux of approximately 9x10$^{-3}$ (mol/m$^2$/d) of carbon dioxide through the unsaturated zone can also be calculated. The CO$_2$ flux is thought to emanate from the ground-water table. The reaction of acidic contaminated ground water with carbonate minerals produces ground waters with high equilibrium partial pressures of CO$_2$ relative to the unsaturated zone atmosphere. The high carbon-13/carbon-12 ($^{13}$C/$^{12}$C) ratios of the unsaturated zone CO$_2$ (as high as -10.75 per mil $\delta^{13}$C with respect to the Vienna Pee Dee Belemnite standard), and the increase in the $^{13}$C/$^{12}$C ratio with increasing CO$_2$ concentrations, suggests that degradation of organic matter and root respiration in the unsaturated zone are not contributing significantly to the CO$_2$ flux. Field measurements show a difference of close to 4.4 per mil in $\delta^{13}$C between the $^{13}$C enriched CO$_2$ sampled just above the water table and CO$_2$ sampled 0.46 meters below the ground surface. A theoretical model constructed assuming (1) steady-state diffusion of CO$_2$ from the water table, (2) a constant $^{13}$C/$^{12}$C flux ratio determined by the isotopic composition of the CO$_2$ exsolving from the water table and (3) a fixed $^{13}$C/$^{12}$C ratio at the ground surface, predicts a difference of close to 4.4 per mil $^{13}$C fractionation between CO$_2$ built up just above the water table and the CO$_2$ coming out of the ground surface. This preliminary model does not, however, satisfactorily explain the field observations, and further research and field data are needed to fully understand our observations.

INTRODUCTION

This paper presents preliminary data gathered at the Pinal Creek toxic-waste site in late November 1991. One of the multiple objectives of this data collection effort was to determine if carbon dioxide (CO$_2$) and oxygen (O$_2$) concentration gradients existed in the unsaturated-zone gas phase. If these gradients existed, we wanted to determine (1) if the unsaturated zone fluxes were at steady state, (2) the magnitude and direction of the fluxes, and (3) the processes responsible for these fluxes. In numerical modelling of multispecies reactive transport at the Pinal Creek site, Glynn and others (1991) had made the assumption that the contaminated phreatic aquifer was open to CO$_2$ exsolution to the unsaturated zone but closed to O$_2$ ingassing from the unsaturated zone. These constraints were forced by the inability of the geochemical codes used to consider reaction kinetics but were conceptually unsatisfactory. Indeed, mass-balance models constructed by Glynn (1991) to simulate the chemical evolution of ground water between wells 51 and 402 invoked both CO$_2$ exsolution and O$_2$ ingassing.

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ACKNOWLEDGMENTS

We are grateful to James Brown and Steve Longsworth for their invaluable assistance in collecting the field data presented in this paper and for providing, together with Ken Stollenwerk, unpublished ground water chemistry data. Ken deserves special commendation for having provided most of the ground-water chemical analyses reported for the Pinal Creek site, all of which are the highest technical quality. We also thank Rosalynd Williams, Jessica Hopple, Julian Wayland and Ray van Hoven for their laboratory analyses of our samples. Finally, the mathematical model presented in this paper could not have been constructed without the extensive help we received from Don Thorstenson and from Edwin Weeks. Weeks raised several criticisms of our $^{13}$C diffusion model. Some of his criticisms, in particular his belief that biological activity could be responsible for the low carbon-13 contents that we measured near the ground surface, will be addressed in a later paper, when more field data are available.

INSTALLATION OF UNSATURATED-ZONE GAS-SAMPLING POINTS

Unsaturated-zone gas-sampling points were installed on November 18, 1991, near the U.S. Geological Survey (USGS) wells at sites 500 and 450 (fig. 1). The sampling points at both sites were installed in the dry Pinal Creek stream bed. The sand and gravel alluvium did not contain any discernible soil zone. The site 450 location floods and new alluvium is redeposited at least once a year. Flooding and sedimentation at the site 500 location probably occurs about once every two years. The first set of gas-sampling points (506U) was installed above a neutralized zone in the ground-water contaminant plume (5.6 < pH < 5.9, high dissolved manganese but low iron concentrations). The other set of unsaturated-zone gas-sampling points (450U) was installed upgradient from 506U, close to the leading edge of the acidic ground-water contaminant plume (4.1 < pH < 4.9, high dissolved manganese and iron concentrations).

Sampling-point set 506U was placed 1.68 m east of ground water well 506. Sets 450UA and 450UB (referred together as 450U) were placed about 1.5 m from each other at the foot of the 2-m-high dry creek bank, about 5.49 m west of wells 451 and 452, which, at the time, were located on the edge of the creek bank. The unsaturated-zone sampling points and wells 451, 452, and 453 were washed away by flash floods in the winter of 1992-93. The water table was 6.11 m below ground surface at well 451 or 4.77 m below ground surface at sites 450UA and 450UB according to a level of the stream bed taken in April 1992 (James Brown, oral commun.). At site 506U, the water table was encountered 2.26 m below ground surface.

Two-inch diameter holes were hand-augered to seven-ft (2.1-m) depth (holes 506U, 450UA) and to 3-ft (0.91-m) depth for hole 450UB. One-eighth of an inch o.d. copper tubes were placed in the holes (at depths of 2.13, 1.80, 1.31, 0.91, and 0.46 m for hole 506U; 2.01, 1.49, 0.82 and 0.42 m for hole 450UA; 0.88 m for hole 450UB). The bottom end of the copper tubes was bent into a loop to ensure that the tube end pointed down but did not constitute the lowermost resting point of the copper tubing. A layer of gravel was placed around each sampling point, followed by a layer of sand, a layer of silica flour, a layer of sand and the next sampling-point gravel layer. Each layer was about 0.08 m deep. The top of the hole was back filled with natural material. The purpose of the silica flour was to act as a less permeable barrier between the various sampling points, ensuring horizontal gas flow from the surrounding soil to each sampling point.

Unsaturated-zone gas sampling at 506U was conducted in the late afternoon on November 22 and at 450UA and 450UB in the morning of November 23 (morning air temperature was at least 5 °C colder than that of the previous afternoon). A quick screening of CO$_2$ partial pressure was conducted for each sampling tube. After verifying that the tubes allowed the easy flow of soil gas, brass Swedgelock fittings and caps were placed on the top ends of the copper tubes, and the sampling-point installations were allowed to re-equilibrate to background soil conditions.

Unsaturated-zone gas sampling at 506U was conducted in the late afternoon on November 22 and at 450UA and 450UB in the morning of November 23 (morning air temperature was at least 5 °C colder than that of the previous afternoon). A quick screening of CO$_2$ partial pressure was conducted for each sampling tube. After a 300-cm$^3$ purge, 300-700 cm$^3$ of soil gas (depending on CO$_2$ concentration) were passed through a Dräger CO$_2$ indicator tube. These field screening results are not presented here because they were much less accurate than the laboratory gas-analysis results.

A stainless-steel pump was used to sample soil gas. After the initial screening, and after an initial three-minute purge of each unsaturated zone tube (flow rate: 500 cm$^3$/min), two 500 cm$^3$ gas samples (for carbon 13 and major gas analyses) were collected in glass sampling tubes.
Figure 1. Area of study (Site 506U is next to well group 500, site 450U is next to well group 450).
CARBON DIOXIDE FLUX

CO₂ concentrations varied from 0.1 to 1.1 volume percent (fig. 2A). Although these values would not be particularly large for a normal soil, the absence of any noticeable soil zone at the sites and the increasing content with depth suggest an external source of CO₂. A linear fit of the data from 506U gave a slope of 0.429 ± 0.026 (standard error) volume percent of CO₂ per meter of depth with an intercept of 0.17 ± 0.03 percent CO₂ at ground surface, significantly higher than the atmospheric value of 0.035 percent.

Carbon-13 results are shown in figs. 2B and 2C; δ¹³C is given in standard notation in per mil with respect to the Vienna Pee Dee Belemnite standard, and was calculated as follows:

\[ \delta^{13}C = \frac{R - R_{\text{std}}}{R_{\text{std}}} \times 1000 \]

where \( R \) and \( R_{\text{std}} \) are the \(^{13}\text{C}/^{12}\text{C} \) concentration ratios in the sample and in the standard, respectively.

The \( \delta^{13}C \) values range from -10.75 to -15.15 per mil at sampling-point site 506U (for a difference of 4.4 per mil) and from -16.8 per mil to -18.45 per mil at site 450U. Linear regression of the data gives slopes of 2.69 ± 0.13 per mil per meter of depth at site 506U, and 0.966 ± 0.28 at site 450U. An extrapolated \( \delta^{13}C \) value of -14.1 per mil at the water table, approximately 4.78 m below ground, was calculated for sites 450UA and 450UB, resulting in a \( \delta^{13}C \) difference of 4.6 ± 1.3 per mil between the water table and the ground surface. The measured \( \delta^{13}C \) values appear to change linearly as a function of depth (fig. 2B) and CO₂ (fig. 2C). However, steady-state diffusion of ¹²CO₂ and ¹³CO₂ would imply curved \( \delta^{13}C \) profiles as a function of depth and CO₂ (dashed lines in figs. 2B and 2C). The curved lines drawn were calculated assuming a linear variation in ¹²CO₂ and ¹³CO₂ concentration with depth between the deepest and shallowest sampling points at each site.

The measured \( \delta^{13}C \) values and their increase with depth, the linear increase in CO₂ concentrations, the absence of vegetation cover, and the absence of a visible soil zone, indicate that the origin of the unsaturated-zone CO₂ is probably not of biogenic origin, particularly at sampling-point site 506U. Indeed, Parada and others (1983) report \( \delta^{13}C \) values of -18 to -20 per mil for soil CO₂ in the Tucson basin (at about 800 m elevation). They attribute the source of their soil CO₂ primarily to the decomposition of organic matter and root respiration (\( \delta^{13}C = -26 \) per mil for plants using the C₃ photosynthetic cycle (also known as the Calvin cycle) and \( \delta^{13}C \approx -13 \) per mil for plants with the CAM (Crassulacean Acid Metabolism) photosynthetic cycle). They believe that mixing with atmospheric CO₂ (\( \delta^{13}C = -8.5 \) per mil), and possibly evaporation of water (resulting in the precipitation of caliche (−3.5 per mil) and the release of CO₂ (−20.5 per mil), also are occurring. Parada and others (1983) report that vegetation in their study sites was dominated by C₃ plants, with a maximum of 20 to 30 percent CAM plants at one site. Soil CO₂ at that particular site had correspondingly heavier \( \delta^{13}C \) values (−17 to −13 per mil).

In contrast with our study, Parada and others (1983) observed a decrease, instead of an increase, in \( \delta^{13}C \) with depth and with increasing CO₂ concentration. Parada and others attributed this effect to mixing with atmospheric CO₂ and to the shallower roots of CAM plants relative to those of C₃ plants. The higher \( \delta^{13}C \) values measured in our study, compared to those measured by Parada and others, are another indication that biogenic CO₂ production (from respiration and/or organic matter degradation) is not a dominant process in our study sites.

The linearity of the CO₂ concentrations with depth indicates that a process of steady-state diffusion of CO₂ through the unsaturated zone may be operative at the unsaturated-zone sites, particularly at 506U where we were able to auger down to the water table. Cerling and others (1991) have described the carbon-isotope fractionation resulting from the diffusion of CO₂, produced throughout a soil zone. Cerling and others measured a difference of 4.4 per mil in carbon-13 content between soil CO₂ (sampled at 50-cm depth in montane soils with a range of soil isotopic compositions) and respired CO₂ (sampled coming out of the soil). Cerling and others attributed this fractionation to the greater diffusivity of ¹²CO₂ relative to that of ¹³CO₂, the diffusion coefficients of these two molecules being related by the following equation (Craig, 1953; Jost, 1960):

\[ \frac{D^{12}}{D^{13}} = \frac{M^{12} + M^{air}}{M^{13} + M^{air}} = 1.0044 \]

where \( D^{12} \) and \( D^{13} \) are the diffusion coefficients of ¹²CO₂ and ¹³CO₂, \( M^{12} \) and \( M^{13} \) are the molecular weights of ¹²CO₂ and ¹³CO₂, and \( M^{air} \) is the average molecular weight of air.
Figure 2. (A) Volume fraction of carbon dioxide in the unsaturated-zone gas phase as a function of depth. Linear regression fits are drawn for sites 506U (long-dashed lines) and 450U (short-dashed lines) in graphs A and D. (B) Carbon isotope composition ($\delta^{13}C$ values in per mil with respect to the Vienna Pee Dee belemnite standard) of unsaturated-zone CO$_2$ gas as a function of depth. The dashed lines in graphs B and C represent the theoretical steady-state lines between lowermost and uppermost points where both CO$_2$ and $\delta^{13}C$ measurements are available. Assuming constant diffusion coefficients, if steady-state diffusion was the only operative process causing CO$_2$ flux between the lower and uppermost sampling points, all $\delta^{13}C$ values measured between these points should plot on the dashed lines in graphs B and C. (C) Carbon-isotope composition as a function of CO$_2$ volume fraction. (D) Volume fraction of oxygen in the unsaturated-zone gas phase as a function of depth.
Under steady-state conditions, the fluxes of $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ through the unsaturated zone must be constant. If the $^{12}\text{CO}_2$ concentration at the ground surface is significantly lower (by a factor of 20 or more) than the maximum concentration in the unsaturated zone near the water table, we predict that there should be a carbon-13 fractionation of close to 4.4 per mil between the $^{13}\text{CO}_2$ present just above the water table and the $^{12}\text{CO}_2$ exiting at the ground surface. This fractionation should be independent of the depth of the unsaturated zone and of the $^{12}\text{CO}_2$ concentration gradient. In addition, under steady-state conditions, the $^{12}\text{CO}_2$ leaving the unsaturated zone must have the same $^{13}C/^{12}C$ ratio as the $^{13}\text{CO}_2$ entering the unsaturated zone from the water table, if no other production source or sink of $^{12}\text{CO}_2$ is present. These statements are described in the following mathematical model.

At steady-state, the diffusive transport of $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ driven purely by a concentration gradient is expressed by the following relations (Fick's first law of diffusion):

$$J^{12} = D^{12} \frac{C^{12}_{wt} - C^{12}_{gs}}{l}$$  \hspace{1cm} (2)

$$J^{13} = D^{13} \frac{C^{13}_{wt} - C^{13}_{gs}}{l}$$  \hspace{1cm} (3)

where $J^{12}$ and $J^{13}$ are the fluxes of $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ through the unsaturated zone, $D^{12}$ and $D^{13}$ are the diffusion coefficients for these two molecular species, $C^{12}_{wt}$ and $C^{13}_{wt}$ are their concentrations in the gas phase just above the water table, $C^{12}_{gs}$ and $C^{13}_{gs}$ are their concentrations at the ground surface, and $l$ is the depth of the unsaturated zone. The capillary fringe is assumed to have negligible thickness.

Furthermore, given that the concentrations of $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ are constant and very small in air, there will be a positive flux of both $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ from the unsaturated zone into the atmosphere, and the two fluxes can be related to each other by the boundary condition

$$J^{13} = J^{12} R_{\text{flux}}$$  \hspace{1cm} (4)

where $R_{\text{flux}}$ is the $^{13}C/^{12}C$ ratio of the $^{12}\text{CO}_2$ entering the unsaturated zone gas-phase. Assuming the system is at steady-state, the fluxes of $^{13}\text{CO}_2$ and $^{12}\text{CO}_2$ leaving the system must equal the fluxes entering the system and, therefore, $R_{\text{flux}}$ must also be equal to the $^{13}C/^{12}C$ ratio of the $^{12}\text{CO}_2$ leaving the unsaturated zone.

We assume that $^{12}\text{CO}_2$ production at the water table is the only net source of $^{12}\text{CO}_2$ in the unsaturated zone and that the atmosphere provides the only net $^{12}\text{CO}_2$ sink.

Combining equations 1, 2, 3 and 4 and defining $R_{\text{wt}}$ as the ratio of the $^{13}\text{CO}_2$ to $^{12}\text{CO}_2$ concentrations just above the water table and $R_{\text{gs}}$ as the ratio at the ground surface leads to the following relation:

$$\frac{R_{\text{wt}}}{R_{\text{flux}}} = 1.0044 + \frac{C^{12}_{gs}}{C^{12}_{wt}} \left( \frac{R_{gs}}{R_{flx}} - 1.0044 \right) \quad \text{(5)}$$

If the $^{12}\text{CO}_2$ concentration at the ground surface is zero, equation 5 shows that there will be a carbon-isotope fractionation of 4.4 per mil between the $^{12}\text{CO}_2$ built up just above the water table and the $^{12}\text{CO}_2$ exiting at the ground surface. If the $^{13}C/^{12}C$ ratio at the ground surface ($R_{gs}$) is more than 1.0044 times the ratio of the $^{12}\text{CO}_2$ leaving the unsaturated zone ($R_{\text{flux}}$) -- that is, if the $\delta^{13}C$ value at the ground surface is greater than the $\delta^{13}C$ value of the $^{12}\text{CO}_2$ entering or leaving the unsaturated zone by more than approximately 4.4 per mil -- the $\delta^{13}C$ value of the $^{12}\text{CO}_2$ just above the water table should be more than 4.4 per mil heavier than the $\delta^{13}C$ of the $^{12}\text{CO}_2$ leaving (or entering) the unsaturated zone:

$$R_{\text{gs}} > 1.0044 \Rightarrow \frac{R_{\text{wt}}}{R_{\text{flux}}} > 1.0044 \quad \text{(6)}$$

or approximately in terms of $\delta^{13}C$ values,

$$\delta_{gs} - \delta_{\text{flux}} > 4.4 \Rightarrow \delta_{wt} - \delta_{\text{flux}} > 4.4 \quad \text{(7)}$$

The opposite relations to equations 6 and 7 also apply. Because the $^{12}\text{CO}_2$ concentration at the ground surface is presumed to be lower than the concentration at the water table, $R_{\text{wt}}/R_{\text{flux}}$ will always be positive.

Our field measurements show a difference of close to 4.4 per mil in $\delta^{13}C$ between the $^{13}C$-enriched $^{12}\text{CO}_2$ sampled just above the water table and $^{13}C$-enriched $^{12}\text{CO}_2$ sampled 0.46 m below ground surface. Unfortunately, the theoretical model constructed above predicts a difference of 4.4 per mil between the $^{12}\text{CO}_2$ built up just above the water table and the $^{12}\text{CO}_2$ exiting at the ground surface. Also, the $\delta^{13}C$ value of the $^{12}\text{CO}_2$ sampled at 0.46 m depth (-15.15 per mil at 506U, -18.45 per mil at 450U) is quite different from the
atmospheric value of -8.5 per mil. There must be some layer near the ground surface in which the CO2 fluxing through the unsaturated zone mixes with atmospheric CO2. Given the lack of data and understanding on the processes occurring at this interface, further research is indicated before our observations can be reconciled with a theoretical model.

The fluxes of CO2 and O2 can be estimated from our measurements at sites 506U and 450U. The concentrations of CO2 and O2 can be calculated from our measured gas volume percentages by the following equation (Thorstenson and others, 1983), assuming an ideal gas:

\[
C_i = \frac{n_i}{V} = \frac{X_i P_{\text{tot}}}{RT}
\]

where \(C_i\) is the concentration of gas \(i\) in moles per cubic centimeter; \(n_i\) is the number of moles of \(i\); \(V\) is the volume of gas in cubic centimeters; \(X_i\) is the mole fraction of gas \(i\) (for ideal gases, \(X_i\) is also equal to the volume fraction of \(i\)); \(P_{\text{tot}}\) is the total atmospheric pressure in atmospheres (atm) and, for an elevation of 900 m (at sites 450 and 500), \(P_{\text{tot}}\) is equal to 0.90 atmospheres, \(R\) is the gas constant (equal to 82.05 cm^3-atm per mol per degree Kelvin); and \(T\) is the temperature, in degrees Kelvin.

Diffusion coefficients for gases in porous media can be estimated from their values in air by various relations accounting for the air-porosity of the medium and its tortuous nature (Thorstenson and others, 1983; Troeh and others, 1982). Our estimation uses the empirical equations developed by Reardon and Muddel (1985) from CO2 and O2 diffusion experiments on uranium mine tailings:

\[
D_{\text{co}_2} = 0.155 \left[ (\varepsilon - 0.05)/0.95 \right]^{1.7}
\]

\[
D_{\text{o}_2} = 3.98 \times 10^5 \varepsilon^{3/2} \left[ (\varepsilon - 0.05)/0.95 \right]^{1.7}
\]

Equations 9 and 10 were tested by Reardon and Muddel (1985) for a range of air-filled porosities, \(\varepsilon\) (from 0.06 to 0.44). From specific yields calculated for the Pinal Creek site (Don Poole, U.S. Geological Survey, written commun., 1993), we estimate an average air-filled porosity of about 0.18 ± 0.02. Using equations 9 and 10, the estimated diffusivities are 5.3 \(10^{-3}\) and 7.0 \(10^{-3}\) cm^2 s^{-1} (centimeters squared per second), respectively, for CO2 and O2.

At site 506U, the estimated CO2 gas fraction just above the water table at 2.26 m is 1.14 percent compared to an average atmospheric CO2 content of 0.035 percent in 1991 (Rowland, 1991). Analysis of dissolved gas in water from well 503, which is screened from 24 and 23.5 m deep, gives an equilibrium pCO2 of 0.103 atm (Glynn and Busenberg, 1996) -- a value 9 times greater than the unsaturated zone pCO2 just above the water table. The estimated CO2 flux at 506U at 25 °C can be calculated from Fick's first law of diffusion (see eq. 2) and equation 8:

\[
J_{\text{co}_2} = D_{\text{co}_2} \frac{(X_{\text{wt}} - X_{\text{air}}) P_{\text{tot}}/R/T}{l} = 5.61 \times 10^{-3} \left(1.143 - 0.035\right) 0.90/100/82.05/298/225
\]

\[
= 1.01 \times 10^{-3} \text{ (mol/cm}^2\text{/s)}
\]

\[
= 8.81 \times 10^{-3} \text{ (mol/m}^2\text{/d)}
\]

The calculation assumes a constant air-filled porosity throughout the unsaturated zone and, therefore, a constant diffusivity. A constant temperature of 25 °C and no temperature-driven diffusive transport also are assumed. The flux values calculated in this paper are believed to be accurate within a factor of 2, primarily because of the uncertainties in the applicable diffusion coefficients.

At site 450U, the estimated CO2 gas fraction just above the water table at 4.77 m is 2.6 percent and the estimated flux is 1.1 \(10^{-11}\) (mol/cm^2)/s or 9 \(10^{-3}\) (mol/m^2)/d. Given the uncertainty in the applicable porosity and the applicable diffusivity, the fluxes calculated for sites 506U and 450U are very close to each other. Analysis of dissolved gas in water from well 452, screened from 8.23 and 5.18 m deep, gives an equilibrium pCO2 of 0.0705 atm CO2 (Glynn and Busenberg, 1996) -- a value 2.7 times the estimated unsaturated zone pCO2 just above the water table.

The ground-water pCO2 values calculated from dissolved-gas analyses are greater than those measured in the unsaturated zone and agree with our hypothesis that the ground water is the primary source of CO2 in the unsaturated zone. The relatively high pCO2 values in ground water are thought to result from the reaction of contaminated acidic ground water with carbonate minerals present in the alluvial aquifer.
and in the underlying consolidated basin fill. CO₂ is probably not actively bubbling out from depth. Indeed, every meter in depth below the water table is equivalent to an overpressure of 0.0968 atmospheres. Data on dissolved N₂, CO₂, O₂ and Ar (Glynn and Busenberg, 1996) in water from wells 503 and 452 indicate that 1.2 to 2.1 m of water depth is sufficient to keep gases from exsolving. The calculation assumes that gas-bubble nucleation is not a limiting factor. Also, the actual movement of exsolved gas bubbles towards the water table would probably be restricted by surface adhesion onto aquifer materials. Evaporation of water could be contributing CO₂ to the unsaturated zone -- a possibility mentioned by Parada and others (1983). The importance of this process, however, remains uncertain because the chemical and isotopic composition of the water at the water table and in the unsaturated zone are not known. Evaporation is generally not thought to be important below 2 m depth in the unsaturated zone (W. Wood, U.S. Geological Survey, written commun., 1993).

The average total carbon concentration of groundwaters at wells 501, 506 and 452 in November 1991 was 6 \(10^{-3}\) mol of carbon per liter of water. The average equilibrium pCO₂ calculated from the pH and composition of the ground waters was 0.12 atm -- a value close to the dissolved gas concentration measured in water from well 503. If the upper 1 m of water at the water table is capable of contributing CO₂ to the unsaturated zone, and if the water-filled porosity is 0.25, we calculate, given the average ground-water linear velocity of 5 m/d (Eychaner, 1989), that 7.5 mol of carbon per day will flow past a 1-m x 1-m x 1-m unit volume below the water table and 9 mmol of carbon per day (or 0.1 percent of the ground-water carbon through-flow) will be transferred from that unit volume into the unsaturated zone.

**OXYGEN FLUX**

The O₂ volume fraction in unsaturated-zone gases decreased as a function of depth at sites 506U and 450U (fig. 2D), although the decrease was not as linear as the CO₂ increase with depth. The extrapolated O₂ gas fraction just above the water table at site 506U was 19.97 percent. The Committee on Extension to the Standard Atmosphere (1976) cites an atmospheric value of 20.95 percent. Therefore the estimated O₂ flux from the atmosphere into the water at 506U is \(1.1 \times 10^{-11}\) (mol/cm²)/s or \(1.0 \times 10^{-2}\) (mol/m²)/d.

The estimated O₂ volume fraction just above the water table at 450U was 18.28 percent. Therefore, the estimated O₂ flux from the atmosphere into the water at 450U is \(1.4 \times 10^{-11}\) (mol/cm²)/s or \(1.3 \times 10^{-2}\) (mol/m²)/d. This oxygen flux is probably caused by the reaction of dissolved oxygen with reduced manganese and iron in the ground water. Indeed, rinds and grain coatings of iron oxyhydroxides and manganese oxyhydroxides are commonly found near the water table (Longsworth and Taylor, 1992; Brown, 1990; Eychaner and others, 1989). Water from wells at site 450 typically had high dissolved manganese and iron concentrations in November 1991, whereas water from shallow wells at site 500 had high manganese but low iron concentrations and, therefore, a much smaller capability for oxygen reduction. Given that dissolved manganese also oxidizes much more slowly than iron, it was reasonable to expect a higher flux of O₂ at site 450U relative to that calculated for site 506U.

The calculated fluxes of O₂ and CO₂ are of similar magnitude with opposite directions. This is consistent with the assumption of a constant total pressure throughout the unsaturated zone. A gradient in total pressure would require consideration of advective fluxes in addition to the diffusive fluxes calculated in this paper. Temperature and barometric pressure at the time of sampling might be partly responsible for differences in the CO₂ and O₂ concentration-depth profiles between sites 506U and 450U, at least at shallow depths, but this factor needs further investigation.

**SUMMARY AND CONCLUSIONS**

CO₂ and O₂ concentration gradients and a gradient in the δ¹³C values of the CO₂ were observed in the unsaturated-zone gas phase at two sites in the Pinal Creek Basin in late November 1991. One unsaturated-zone site (450U) was installed close to the leading edge of the acidic ground water contaminant plume (pH 4.1 - 4.9 and high dissolved manganese and iron concentrations). The other site (506U) was installed above a neutralized zone of the ground water contaminant plume (pH 5.6 - 5.9 and high dissolved manganese but low iron concentrations).

The linearity of the CO₂ concentration-depth relation suggests a steady-state flux of CO₂ out of the unsaturated zone. The increase in δ¹³C values with
increasing CO₂ concentrations, the lack of an observable soil zone, and the fact that the ground waters below the unsaturated zone sites have pCO₂ values several times higher than the unsaturated zone values, indicate that the ground water, rather than degradation of organic matter and(or) root respiration throughout the unsaturated zone, may be the primary source of the observed CO₂. Sampling during a different season and at a different alluvial site above uncontaminated ground water will help verify this conclusion.

Our field measurements show a difference of about 4.4 per mil in δ¹³C between the ¹³C enriched CO₂ sampled just above the water table and CO₂ sampled 0.46 m below the ground surface. A theoretical model was constructed assuming (1) steady-state diffusion of CO₂ from the water table, (2) a constant ¹³C/¹²C flux ratio determined by the isotopic composition of the CO₂ exsolving from the water table and (3) a fixed ¹³C/¹²C ratio at the ground surface. The model predicts a difference of close to 4.4 per mil ¹³C fractionation between the CO₂ built up just above the water table and the CO₂ exiting at the ground surface (with a δ¹³C value different from that of CO₂ at the ground surface). The δ¹³C value of the CO₂ sampled at 0.46 m depth (-15.15 per mil at 506U, -18.45 per mil at 450U) is quite different from the atmospheric value of -8.5 per mil. We conclude that there must be some boundary zone near the ground surface in which the CO₂ fluxing through the unsaturated zone is mixed with atmospheric CO₂. Given the lack of data and understanding on the processes occurring close to the ground surface, further research is indicated before our observations can be reconciled with a theoretical model.

The estimated flux of CO₂ leaving the ground water is about 9 x 10⁻³ (mol/m²)/d at both well sites. This flux is reasonably small compared to the horizontal flux of dissolved inorganic carbon at the water table.

Estimates of the flux of O₂ entering the ground water range from 1.0 x 10⁻² (mol/m²)/day at site 506U and 1.3 x 10⁻² (mol/m²)/day at site 450U. The greater estimated flux at site 450U may be significant given the comparatively high dissolved iron concentrations in ground water at site 450.

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Interactions between Shallow Ground Water and Surface Water that Affect Metal Transport in Pinal Creek, Arizona

By Judson W. Harvey¹, Christopher C. Fuller¹, and Brian J. Wagner¹

Abstract

Solute transport was investigated in shallow ground water and surface water along a 500-meter (m) reach of the perennial stream in Pinal Creek basin. A bromide tracer injection in the stream was conducted to quantify ground-water inflow and streamwater/streambed-water exchange. Respective gains and losses in iron (Fe) and manganese (Mn) in solution occurred in ground water discharging laterally through bank seeps into the stream, and not in ground water discharging vertically from below the active channel, or in the active surface channel itself. Aqueous metal concentrations measured in shallow ground water varied significantly with position across the narrow channel at Pinal Creek. Concentrations of Fe were twentyfold to fiftyfold higher in shallow ground water discharging laterally through channel banks compared to ground water discharging vertically from beneath the stream. Mn was 25 percent lower in bank seepage compared to subchannel ground water. Cross-channel variability in metal concentrations in contaminated ground water could not be explained by differential dilution of ground water discharging laterally to the channel versus vertically through the streambed. Mass-balance calculations for the 500-m reach of stream and shallow aquifer verified that Fe and Mn dynamics in bank seepage were sufficient to affect downstream concentrations of those constituents. Microbial processes in channel banks are hypothesized to drive reductive dissolution of solid phase Fe in ground water discharging laterally through banks, but not in subchannel ground water. The mechanism of Mn loss in this channel reach appeared to be sorption of Mn²⁺ on Fe-oxyhydroxides, which form where ground water emerges from bank seeps.

INTRODUCTION

Shallow ground water that surrounds the active channel of streams is referred to in this paper as the near-stream zone. Basin ground water discharges through the near-stream zone into the channel of gaining (effluent) streams (fig. 1a). In addition to an influx of ground water from the basin, the near-stream zone receives localized recharge fluxes of streamwater (fig. 1b). Mixing of basin ground water and streamwater in the near-stream zone and resulting chemical reactions are hypothesized to be an important control on solute chemistry of surface water in streams (Triska and others, 1993). Redox chemistry is commonly an important factor because of the tendency for a reducing

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zone to develop in the near-stream zone. Resulting chemical reactions in the near-stream zone could affect nutrient and contaminant inflows to streams and, thus, may affect downstream surface-water quality (Peterjohn and Correll, 1986). An ability to quantify and model near-stream hydrological and chemical processes is critical to improving an understanding of the timing and attenuation of nonpoint-source contaminant inflows through shallow aquifers into streams.

In this paper, the chemical reactions in a coupled stream/near-stream system in a basin where groundwater is contaminated by acidic mine drainage are described. The objective of the research was to determine the importance of stream-shallow subsurface-water interactions to metal transport in groundwater and surface water and to downstream water quality in Pinal Creek basin. Contaminated groundwater that presently discharges to Pinal Creek is a calcium sulfate-type water that has high Mn concentrations, somewhat lower concentrations of other metals (Ni, Co, Cu, Fe among others), and higher pH than contaminated water in the acidic core of the plume (Brown and Harvey, 1996). A preliminary experiment was conducted at Pinal Creek in November 1992 to investigate whether a mass-balance approach could quantify attenuation of Mn, Fe and other trace metals along a transport pathway from shallow groundwater into surface water. Preliminary results are reported; the approach will ultimately be used to quantify a net “effective” rate of biologically and chemically driven reactions in the system. The mass-balance approach compliments other research at Pinal Creek aimed at identifying specific chemical reactions at Pinal Creek (Lind and Hem, 1993; Fuller, 1996).

**STUDY SITE AND METHODS**

During low-flow periods without rainfall, streamflow in Pinal Creek basin begins 6 kilometers (km) above Inspiration Dam (fig. 2). The active surface channel meanders in an unbraided channel over a streambed composed of coarse sand and fine gravel; the average streambed slope is approximately 1 percent. We investigated solute transport during November of 1992, a month without significant rainfall at Pinal Creek basin. On November 21, a bromide-labeled-tracer solution was injected into the surface channel near the head of perennial surface flow at a constant rate for 30 hours (fig. 2). Bromide concentrations at downstream monitoring points were used to compute streamflow discharge and net groundwater influx to the channel by the tracer-dilution method (Kilpatrick and Cobb, 1985). Concurrent with the tracer experiment, we collected and filtered water samples from subchannel groundwater (to a depth of 1 m), surface water in the active channel, and in surface outflow from bank seeps and small tributaries (fig. 2). Methods for sample collection and analysis of metal concentrations are reported in Harvey and Fuller (1996). In addition, streamflow data and monitoring of bromide-tracer concentrations were used as the basis for a transient simulation of bromide transport to estimate stream solute-transport characteristics. A nonlinear least-squares optimization approach was used to determine stream and storage zone cross-sectional areas, a dispersion coefficient, and a mass-transfer coefficient between the stream and “storage zones” (Wagner and Harvey, 1996).

**BROMIDE TRACER INJECTION TO DETERMINE GROUND-WATER INFLUX AND STREAMWATER/STREAMBED-WATER EXCHANGE**

Ground-water influx and streamwater/streambed-water exchange fluxes were estimated from the bromide-tracer-dilution measurements. Lateral inflow of ground water in the first 500 m of streamflow accounted for 35 percent of all groundwater inflow to the entire 6-km stream reach upstream of Inspiration Dam; this computation is based on comparison of computed ground-water inflows with streamflow measured at Inspiration Dam.

Bromide tracer concentration histories in the stream were simulated with a one-dimensional stream transport model with lateral ground-water inflow and solute exchange with storage zones (Wagner and Harvey, 1996). Characteristics of the modeled solute storage zones determined for Pinal Creek differed from values previously determined for higher-gradient, gravelbed streams. For example, the ratio of the cross-sectional area of the storage zone to that of the active channel at Pinal Creek (between sites 1 and 2) is about 0.2, compared to ratios which are typically 10 times higher in gravelbed pool and riffle streams with higher gradients (Broshears and others, 1993). This result suggests that the zone of transient storage of streamwater solutes in the subsurface (fig. 1b) might be smaller in low gradient sandbed streams compared to higher gradient gravelbed streams.
Figure 2. Locations of ground-water and surface-water sites sampled during the solute-transport study, November 1992.

The simulation cannot determine where storage is occurring—that is, along channel margins where recirculating zones are present, or in the subsurface. However, the presence of bromide-labeled water at shallow depths (up to 6 centimeters (cm)) in the streambed indicates that streamwater is in contact with more sediment than the amount exposed on the streambed surface. Sampling in the subsurface supports the hypothesis that transient storage of streamwater solutes might be explained by convective flow of streamwater through the streambed.

Results of the preliminary tracer study indicated that the flux of streamwater through the streambed and contact time of that water with sediment surfaces is significant, and potentially could enhance Mn oxidation. Harvey and Fuller (1996) concluded that most of the Mn oxidation that occurs in Pinal Creek probably is catalyzed on streambed surfaces; thus streamwater/streambed sediment contact times and contact area are likely to be critical controls on Mn loss from solution. At this time we have established only the potential for
a stream–subsurface interaction that could enhance Mn oxidation. Data and observations from November 1992 (Fuller, 1996) suggest that most Mn oxidation occurs in the stream well downstream of the beginning of perennial streamflow where our experiment was conducted. An experiment downstream from site 3 is currently being planned to determine the importance of stream–subsurface water exchange on Mn oxidation at Pinal Creek.

CHEMICAL PROCESSES IN GROUND-WATER INFLOW DURING PASSAGE THROUGH THE NEAR-STREAM ZONE

The mass balance for a solute in a coupled stream–shallow aquifer system is, assuming steady-state conditions,

\[ (C_u Q_u)^i + (C_{gw} Q_{gw})^i - (C_d Q_d)^i + R^i = 0 \]  (1)

where \( i \) indicates the reach of interest, \( C \) is solute concentration (mass/volume), \( Q \) is water flow (volume/time), subscripts \( u \) and \( d \) indicate upstream and downstream ends of reach \( i \), respectively, and \( R \) is a solute reaction rate (mass/time). The subscript \( gw \) refers to reach-averaged solute concentrations and water fluxes in basin ground water that discharges into reach \( i \).

Dilution of contaminated ground-water inflow to the stream with uncontaminated ground water was not expected to be important during base flow recession in this system; however, dilution effects were checked by modeling Na transport. Na in contaminated ground water of the basin fill aquifer is highly concentrated compared to uncontaminated water; the contaminated to uncontaminated ratio of Na concentration in ground water is 4:1 (Glynn, 1991). Na concentrations in inflowing ground water for each reach were computed from equation 1 by using measured water fluxes and concentrations of Na in streamwater. Assuming that transport of Na was conservative, mass-balance calculations demonstrated that contaminated ground water enters the stream without significant dilution by inflow of uncontaminated water. For example, the calculated Na concentrations for ground-water inflow in each subreach is a good approximation to measured concentrations in subchannel ground water and in bank seepage in that reach (fig. 3). The overall variation in measured Na concentrations at all sites is less than 5 percent, including a comparison to Na concentrations measured in deep piezometers (well observation group 500, fig. 2) that penetrate the aquifer to 40 m.

Fe concentrations in subchannel ground water, and in deeper piezometers (well observation group 500, fig. 2) were approximately equal to the Fe detection limit in this system. Fe concentrations in the stream were computed from equation 1 assuming an Fe concentration in inflowing ground water that was equal to the detection limit. Dashed lines in figure 4a connect instream concentrations that were calculated from equation 1, assuming conservative transport. Measured concentrations of Fe in streamflow at sites 1 and 3 were larger than calculated concentrations. A positive difference between measured and calculated concentrations in the stream represents a gain of that metal in solution along the flow path. Figure 4a, therefore, indicates that a gain in aqueous Fe occurred somewhere along the flow path beginning in ground water.

The mass-balance approach cannot specify the exact location of the gain in Fe or the reaction that produces it. Aqueous Fe is hypothetically thought to be produced by reaction in shallow ground water as it discharges laterally through channel banks and into the stream. Detailed measurements along the 500-m reach indicated that Fe concentrations in bank seeps were twentyfold to fiftyfold higher than in subchannel ground water (fig. 4a). Furthermore, the Na balance indicated that higher measured concentrations of Fe in bank seeps cannot be explained by mixing of ground water from contaminated and uncontaminated sources; therefore, ground water passing through bank seeps has virtually the same origin as ground water discharging from directly beneath the active channel. Riparian vegetation is present on channel banks, and organic matter content of sediment appears higher. Microbial respiration in channel bank sediments appears to be lowering the Eh sufficiently to cause reductive dissolution of Fe in channel bank sediments during passage of shallow ground water through the channel banks.

The Mn concentration in ground water emerging from bank seeps was 25 percent less than in subchannel ground water. The mass balance for Mn assumed conservative transport; concentrations of Mn in ground water for each reach were computed from a best-fit relation between Mn and Na in subchannel ground water \((r^2 = 0.724, n = 24)\). Mn concentrations predicted by mass balance matched measured concentrations of Mn in the stream quite well except at site 2, where the measured Mn concentration was larger than the concentration predicted by the mass balance (fig. 4b). The mass balance indicates loss of Mn from solution in shallow ground water or in streamflow in the
Figure 3. Sodium concentrations in shallow ground water and surface water as a function of downstream distance from the head of streamflow at Pinal Creek.
Figure 4. Variation in iron and manganese concentrations in streamflow, subchannel ground water, ground water discharging from bank seeps, and small tributaries at Pinal Creek, (A) iron, (B) manganese.
reach between sites 1 and 2. Lower Mn concentrations in bank seepage compared to subchannel ground water or the stream suggests that Mn loss occurs in shallow ground water as the water passes through bank seeps. This supposition is supported by observations that oxidation of Mn occurs slowly, if at all, in streamflow in the first 500 m of perennial streamflow in Pinal Creek (Eychaner, 1991; Harvey and Fuller, 1994, this report).

Mn transfer to the solid phase appears, therefore, to be occurring by precipitation in shallow ground water at some point during the passage through bank seeps. Some of the filterable Fe that is gained by dissolution in channel banks oxidizes and forms Fe flocs at the point of discharge of shallow ground water from bank seeps. Fe oxides may be sorbing Mn, and (or) acting as a catalyst for oxidation of Mn (Davies and Morgan, 1989), which could account for the low Mn concentrations in bank seepage compared to Mn concentrations in subchannel ground water, and for the loss of Mn from solution in the stream reach between sites 1 and 2.

SUMMARY

The solute transport in 500-m reach of stream and shallow aquifer immediately downstream of the beginning of perennial streamflow was studied. A 30-hour instream bromide-tracer experiment demonstrated that streamwater/streambed-water exchange increased the area of contact and the contact time of streamwater and stream solutes with bed sediment. Mn oxidation potentially is enhanced by streamwater/streambed-water interactions at sites downstream of the study reach in Pinal Creek. In the study reach, Fe dissolution and Mn precipitation occur in shallow ground water as it passes through channel-bank sediments prior to discharge into the stream. The Fe concentration was twentyfold to fiftyfold higher and Mn was 25 percent lower in bank seepage compared to concentrations discharging from deeper within the aquifer and in ground water discharging directly beneath the streambed. Comparatively higher organic matter content and bacterial metabolism in bank sediments appears to drive reductive dissolution of Fe. Mn probably sorbs or coprecipitates with Fe oxides that precipitate as the water seeps from the channel sides. These reactions do not occur directly beneath the channel. Data on the chemistry of subchannel ground water, streamwater, and bank seepage will be used, along with the mass-balance model, to constrain the magnitude of reactive chemical processes in perennial flow.

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Association of Selected Metals with Colloidal and Suspended Particulate Material in Shallow Ground Water and Surface Water at Final Creek, Arizona

By Judson W. Harvey and Christopher C. Fuller

Abstract

Trace metals are potentially transportable as solid phases in ground water and surface water in association with colloids or suspended particulates. Field data that specifies the partitioning of metals between dissolved and suspended solid phases is necessary for developing physically based models of metal transport. The purpose of the present study was to determine colloidal and suspended-particulate concentrations for selected metals in shallow ground water and in streamflow of the perennial reach of Final Creek during base-flow conditions. Concentrations of manganese (Mn), iron (Fe), nickel (Ni), copper (Cu), and cobalt (Co) were measured in unfiltered water samples, and compared with 0.45 μm (micrometer) and 0.001 m filtrates of the same water samples. Total metal concentrations in unfiltered water were partitioned into suspended particulate (>0.45 μm), colloidal (0.001 - 0.45 μm), and dissolved (<0.001 μm) components. Median colloidal and suspended-particulate concentrations for Mn, Ni, Cu and Co were several percent or less of total concentrations of those metals. In contrast, the sum of Fe colloidal and suspended-particulate phases was a large percentage of total Fe concentrations in some cases, which indicated that a colloidal or particulate Fe phase was significant at Pinal Creek. At present total Fe concentrations in suspension are low in shallow ground water and in streamflow at Pinal Creek during base-flow conditions. Colloids that do form do not appear to be significant sorbents of other trace metals, compared to Mn and Fe solid phases on the streambed. Colloid-facilitated metal transport will likely increase in importance if acidic ground water (which has Fe greater than 50 milligrams per liter) reaches Pinal Creek.

INTRODUCTION

Given favorable chemical conditions, colloids or small-diameter particulates can move long distances in suspension in ground water and surface water (see review by McCarthy and Zachara, 1989). Metals that have been partitioned to the solid phase are still transportable under such conditions if adsorbed to colloidal matter (Ryan and Gschwend, 1990; Penrose and others, 1990). Colloids are commonly formed by precipitation of Fe hydrous-metal oxides in contaminated water, including sewage-contaminated ground water (Langmuir, 1969) and streams contaminated by acidic mine drainage (Kimball and others, 1992). Fe colloids are also observed in natural ground waters (Ryan and Gschwend, 1990). High concentrations of Mn are associated with acidic mine drainage (Wentz, 1974), and Mn colloids are occasionally observed (Hart and others, 1992). However, Mn colloids can be less common than Fe colloids in systems affected by acidic mine drainage, because of the kinetic limitation on oxidation of Mn$^{2+}$ (Hem, 1981; Davies and Morgan, 1989). Because of the strong ability of Fe and Mn oxides to scavenge other dissolved metals at Pinal Creek (Lind and Anderson, 1992), transport of many metals depends on...
whether Fe and Mn oxides form as colloids or coatings on streambed sediment (Kimball and others, 1992).

The history of contamination at Miami Wash and lower Pinal Creek basin, Arizona is summarized in Brown and Harvey (1996). Briefly, acidic mine waste water infiltrated from a holding pond into alluvium of Miami Wash and has moved 15 km downgradient in the subsurface into the Pinal Creek basin. Initially during transport of acidic mine waste water, the low pH favored dissolution and transport of trace metals in the dissolved phase. Acidity was neutralized by carbonate dissolution and mixing with uncontaminated water, which retarded the movement of the steep pH front in the contaminated ground-water plume (Eychaner, 1991a). Iron oxyhydroxides precipitated near the pH front, and functioned as the principal sorbent for Co, Cu, and Ni (Stollenwerk, 1991), which retarded movement of those metals out of the basin. The pH front is presently about 1 km (kilometer) upgradient from the head of perennial streamflow in lower Pinal Creek basin.

Colloid concentrations in ground water are significant near the pH front of the contaminant plume; oxidation of Fe$^{2+}$ near the pH front apparently resulted in formation of Fe colloids (Puls and Eychaner, 1990). Colloid concentrations were much lower at a well site 2 km downgradient from the pH front (Puls and Eychaner, 1990); therefore colloids do not appear to be transported a great distance in ground water at the site. Low colloid concentrations could have resulted from the effects of high ionic strength of contaminated water on colloid mobility. According to theory, high concentrations of Ca$^{2+}$ and other cations increase nonspecific sorption, which destabilizes colloids (Stumm and Morgan, 1981).

Rapid adjustment of pH and pe occurs as shallow ground water is discharged to surface water in Pinal Creek, because of CO$_2$ outgassing and by O$_2$ reaeration (Eychaner, 1991b). Ficklin and others (1991) provided evidence that large quantities of Fe and Mn oxides were forming near the water table at "observation well group 500" in fig. 1, near the head of perennial streamflow. The formation and transport of Fe and Mn colloids at the shallow ground-water-streamflow interface was not previously investigated at the site. Understanding the potential importance of colloids to metal transport in shallow ground water and in streamflow is basic to the research effort in Pinal Creek basin.

### METHODS

Pinal Creek streamflow is perennial in a 6-km reach where ground water is forced to the surface as the alluvial deposit narrows and shallows towards its terminus at Inspiration Dam (fig. 1). Selected metals were sampled in Pinal Creek during November 19-22, 1992 -- a period without rainfall and not preceded by substantial rainfall for several months.

Shallow multilevel samplers were installed vertically in the streambed at three locations in the central channel 1 month before metal sampling began. Locations for multilevel samplers were sites 0, 1, 3 and 5 (fig. 1). Sampler design followed the multilevel sampler design of LeBlanc and others (1991). Sampler ports were located at 100, 50, 25, 12, 6, and 3 cm below the sediment surface. Ground-water samples were pumped through a peristaltic pump at a rate of approximately 200 mL/min. The pump and filtration system was closed from the atmosphere and protected from light to reduce effects of aeration and photoreduction on metal concentrations (Puls and Eychaner, 1990; Ryan and Gswhend, 1990; McKnight and others, 1988).

![Figure 1. Locations of ground-water and surface-water sites sampled during the solute-transport study, November 1992.](image-url)
Prior to collection of raw and filtered samples for metal analysis temperature, specific conductance, dissolved oxygen, pH, and oxidation-reduction potential were measured in a flow cell until values of the measured properties had stabilized. After stabilization occurred, sample flow was redirected to a second flow cell to verify the pH measurement. A sample for the measurement of alkalinity was collected in outflow from the second flow cell by overfilling three bottle volumes before capping.

Following the measurement of above properties, the sample feed tube was disconnected and a raw sample was collected. The sample feed tubing was then connected to two tangential-flow filtration units that were connected in series, with the 0.45 μm pore size membrane preceding the 0.001 μm pore size membrane in the series. The initial filtrate was used to rinse the sample bottles (acid rinsed 125 mL polyethylene bottles) and then discarded. Raw and filtered water samples were acidified with trace-metal-grade HNO₃ to 0.05 equivalents of acid per liter.

Pinal Creek surface water, bank-seeps, and tributaries were sampled at numerous locations along the creek. Sampling was conducted in a manner similar to shallow ground water sampling, except that the flow cell was not used to measure water-quality properties. At those locations pH, temperature, specific conductivity and dissolved oxygen concentration were measured with conventional field meters.

Metal concentrations were measured for all samples using inductively coupled plasma atomic emission spectroscopy (ICP-AES). Total Fe concentration was also determined for selected samples using the ferrozene colorimetric method (Stoakey, 1970). The analytical precision for determining concentrations of each metal was estimated by calculating an average standard deviation from triplicate determinations on each sample. An approximate coefficient of variation (CV) for each metal was calculated by dividing the mean metal concentration by the average standard deviation of triplicate determinations.

Filtration with a 0.45 μm pore-size membrane is routinely used to determine concentrations of dissolved constituents. If colloids are present, the dissolved fraction of metals is overestimated because of passage of colloidal phases through the filter. In order to test for metal-contaminant associations with colloids and suspended particulates in shallow groundwater and surface water the method of sequential filtration of water samples was used (Kennedy and Zellweger, 1974; Laxen and Chandler, 1983; Kimball and others, 1992). Paired water samples were collected at each measurement site: one sample was unfiltered and the other was sequentially filtered through two filter membranes of decreasing size (0.45 μm and 0.001 μm pore size).

Size-class fractions of particulates were operationally distinguished as follows; suspended particulate (>0.45 μm diameter), colloidal (0.001 - 0.45 μm), and dissolved (<0.001 μm) components. Colloidal and suspended-particulate concentrations were calculated as the difference between concentrations in 0.45 μm and 0.001 μm filtrates, and unfiltered and 0.45 μm filtrates, respectively. The analytical precision of colloidal and suspended-particulate concentrations is inflated because of the subtraction of two individual concentrations, each with associated precisions. For present purposes the average precision of a colloidal or suspended-particulate concentration for a particular metal was estimated as,

$$\bar{\sigma}_{\text{col}} = \sqrt{\sigma^2 + \sigma^2}$$

where $\bar{\sigma}_{\text{col}}$ is the average standard deviation of the calculated colloidal or suspended-particulate concentration for a particular metal, and $\bar{\sigma}$ is the average standard deviation of the individual determinations for that metal.

Detection limits for individual determinations of Fe concentrations using ICP-AES were poor, necessitating the use of the colorimetric determinations for calculating Fe colloidal and particulate concentrations. Only five samples were analyzed colorimetrically for Fe, and determinations were done on unfiltered and 0.001 μm filtrates only. Thus only a sum of colloidal and particulate concentrations could be determined for Fe.

**RESULTS**

The potential importance of colloids and suspended particulates is apparent on bivariate plots of metal concentration in filtered water samples as a function of unfiltered samples. In figure 2, concentrations of Ni, Cu and Fe in filtered water samples are plotted as a function of concentrations in unfiltered water. The data plot roughly on an
equivalence line with slope equal to one. The precision envelopes in figure 2 define a region equal to plus or minus a constant percentage of the metal concentration as determined from the coefficient of variation for that metal \( (2CV^2)^{1/2} \). The precision envelopes consider analytical error in both filtered and unfiltered concentrations and are an appropriate guide for roughly evaluating whether data departures from the equivalence line are meaningful. Colloidal and particulate-metal concentrations are potentially important if concentrations plot outside and below a precision envelope surrounding the equivalence line; such a result implies that filtered concentrations are lower than unfiltered concentrations due to the removal of a particulate metal phase during filtration.

Most plotted values in Figures 2a and 2b (for Ni and Cu respectively) plot within the precision envelope for those metals; outliers fall only slightly outside the precision envelope on both sides of the equivalence line. In contrast, all Fe values plot below the precision envelope and some values plot far below it (fig. 2c). Examination of plots for all selected metals investigated in this study (Mn, Ni, Cu, Co and Fe) indicated that only an Fe colloidal and particulate phases was a significant fraction of the total unfiltered concentration for that metal at Pinal Creek.

Colloidal and suspended-particulate concentrations were also examined using box plots (fig. 3). Box plots divide observations into quartiles and the 'notches' demarcate an approximate 95 percent confidence interval for the distribution around the median value. The median colloidal and suspended-particulate Mn concentrations were similar in magnitude to the average precision estimate for those determinations (fig. 3a). For Mn the notches overlap the limit of uncertainty for detecting Mn colloids and suspended particulates; this was also true for Ni, Cu and Co. This general result indicates that colloidal and suspended-particulate concentrations were probably not large enough to be statistically distinguished from zero.

Too few analyses were available to construct a box plot for Fe (fig. 3b). Examining the data directly, four out of five Fe particulate concentrations were above 0.02 mg/L, the analytical precision estimate for an Fe colloidal plus particulate phase, and two of those concentrations were more than ten-fold greater than the analytical detection limit. Fe colloids and suspended particulates therefore appeared to be an important fraction of total Fe concentrations.

![Figure 2](image.png)
**Figure 2.** Metal concentrations in filtered water samples as a function of concentrations in unfiltered samples: (a) Nickel, (b) Copper and (c) Iron.
DISCUSSION

Colloidal and particulate-metal concentrations at Pinal Creek were low relative to dissolved-metal concentrations during base-flow conditions. Fe, Ni and Cu colloidal and particulate-metal concentrations were slightly higher than precision estimates, which implies that some metals are possibly being transported as colloids and suspended particulates. The precision estimates for colloidal and suspended particulate concentrations themselves were relatively high due to the inflation of error that is inherent in calculating colloidal and suspended-particulate concentrations by differences. Results presented here indicate that colloidal and suspended-particulate metal concentrations probably cannot be distinguished statistically from zero at Pinal Creek during base-flow conditions.

Faires and Eychaner (1991) and Eychaner (1991b) reported that metals at Pinal Creek (excluding Fe) are lost from solution in the downstream direction in Pinal Creek. A significant decrease in dissolved concentrations of Mn, Ni and Co concentrations in the downstream direction in Pinal Creek was also observed in November 1992 (Fuller, 1996). The present study demonstrated that the decrease in concentrations of dissolved metals in the downstream direction probably can not be explained by the formation of metal colloids and suspended particulate phases.

Oxidation of Fe$^{2+}$ is a major source of colloids in other shallow ground-water and surface-water systems (Kimball and others, 1992; Ryan and Gschwend, 1990). At the Pinal Creek study site, Fe appeared to be associated with a colloidal and suspended-particulate phase greater than 0.001|μm in diameter. That material probably was colloidal Fe-oxyhydroxides, formed by oxidation of Fe$^{2+}$ in ground water discharging to the stream. The order-of-magnitude higher Fe concentrations in seeps compared to those in ground water beneath the channel bed (Harvey and others, 1996) indicates that the source of Fe in Pinal Creek was discharge from bank seeps; this source is further supported by the observation of Fe flocs at seep inflows.

Mn$^{2+}$ oxidation in natural waters is known to occur at rates several orders of magnitude faster than homogeneous oxidation in solution by dissolved oxygen. The oxidation rate can be enhanced by adsorption of Mn$^{2+}$ onto the surfaces of Fe oxyhydroxides, Al oxides, silica (Davies and Morgan, 1989), and/or newly formed surfaces of Mn oxides (Hem, 1978). If present, Mn colloids are at concentrations of 1 mg/L or less compared to a dissolved concentration of approximately 90 mg/L. Such low concentrations of Mn colloids in Pinal Creek indicates that oxidation of Mn$^{2+}$ throughout the 6-km reach probably occurs primarily through a surface-catalyzed reaction on coatings of bed sediments. Trace metals such as Ni and Co are most likely partitioned to the solid phase by coprecipitation or sorption on Mn oxide and/or carbonate phases on the streambed (Lind and Anderson, 1992).
SUMMARY

The fraction of total Mn, Ni, Cu and Co concentrations in Final Creek as colloidal and suspended-particle material was low during base-flow conditions. Colloidal Fe was a significant fraction of total Fe concentrations in Final Creek, but since total concentrations of Fe in the stream are low at present, the importance of Fe colloids as a sorbent for other metals is at present probably minor compared to Mn and Fe solid phases on the streambed. Chemical conditions at Final Creek also apparently do not favor significant Mn-colloid formation and associated transport of solid-phase trace metals. Fe colloids will likely increase and substantially affect metal transport if the acidic core of the contaminant plume, where the Fe concentrations exceeds 50 mg/L, reaches Pinal Creek.

REFERENCES


Solute-Transport Parameter Estimation for an Injection Experiment at Pinal Creek, Arizona

By Brian J. Wagner and Judson W. Harvey

Abstract

Parameter estimation is an important step in the development of contaminant-transport simulation models. In this paper, we demonstrate an inverse modeling methodology for estimating the transport parameters that characterize the migration, attenuation, and redistribution of contaminants. The inverse model proceeds in two stages: In stage one, a finite difference solute-transport simulation model is coupled with nonlinear least-squares regression to identify the model parameter values that "best" reproduce the measured solute concentrations. In stage two, solute-transport simulation is combined with first-order uncertainty analysis to quantify parameter-estimate uncertainty. The methodology is widely applicable to transport models for ground-water and stream systems; here we demonstrate the application to a stream system. Using data from an injection experiment at Pinal Creek, Arizona, the inverse model is applied to analyze parameters for a one-dimensional solute-transport model with advection, dispersion, lateral inflow, and transient storage. The parameters estimated by the inverse model are dispersion coefficient, stream cross-sectional area, storage-zone cross-sectional area, and stream-storage exchange coefficient. The parameter estimates and associated uncertainties support the interpretation that the transient-storage mechanism is active in Pinal Creek. A discussion of concentration sensitivity to these four estimated parameters is presented to explain how analysis of uncertainties in parameter estimates can be used to identify sampling strategies for reliable parameter estimation.

INTRODUCTION

Toxic substances can be introduced into stream systems through point-source releases of contaminants, overland flow of contaminated water, and/or by subsurface discharge from contaminated ground-water. Because an episode of contamination can affect stream-water and ground-water quality at distant locations, accurate prediction of the movement and redistribution of contaminants is essential. Solute-transport models are valuable tools for investigating the effect of contamination on downstream water quality. However, accurate prediction of the arrival times and distributions of contaminants at specific points in streams is difficult because the true values of the hydrologic and chemical parameters used in the solute transport model are unknown. Direct measurement of these parameters is difficult or impossible, and estimation by trial-and-error calibration does not guarantee that the estimates are optimal nor does it quantify the reliability of the parameter estimates. Our study, which follows the approach of Wagner and Gorelick (1986), uses a statistically based inverse model to estimate transport parameters and quantify the reliability of the estimates. Using data from an injection experiment at Pinal Creek, Arizona, we demonstrate here how the inverse model can be used to identify optimal parameter estimates and analyze estimate uncertainty. We then extend the work of Wagner and Gorelick (1986) to examine how parameter estimate uncertainty analysis can aid in evaluating the value of data for parameter estimation and sampling-network design.
SOLUTE TRANSPORT IN STREAMS

Modeling of contaminant transport must begin with assumptions about the processes that control solute movement and redistribution. Transport modeling in streams typically begins with the one-dimensional advective-dispersive equation. However, the advective-dispersive equation alone does not adequately describe contaminant transport in many small stream systems. For example, solute transport in small streams is commonly characterized by concentration histories which are attenuated and delayed with respect to concentration histories predicted by the advective-dispersive equation (Bencala and Walters, 1983). Solute transport in these streams is affected by dilution by lateral inflow and by exchange of solute between the main channel and a “storage” zone of slow-moving or immobile water at the channel margin or in the subsurface. In this conceptualization, the hydrologic regime is divided into two coupled systems: a system of flowing water in the main stream channel, and a system of storage zones containing immobile water. The two systems are coupled by a mass-transfer mechanism that exchanges solutes between the mobile and immobile regimes. The model for advective-dispersive transport with inflow and transient storage was formulated by Bencala (1984) as

\[
\begin{align*}
\frac{\partial C}{\partial t} &= -\frac{Q}{A} \frac{\partial C}{\partial x} + \frac{1}{A} \left( \frac{\partial}{\partial x} \left( D \frac{\partial C}{\partial x} \right) \right) + \frac{q_l}{A} (C_l - C) + \alpha (C_S - C) \\
\frac{\partial C_S}{\partial t} &= -\alpha \frac{A}{A_S} (C_S - C)
\end{align*}
\]  

where

- \( C \) is solute concentration in the stream (mg L\(^{-1}\)),
- \( Q \) is volumetric flow rate (m\(^3\) s\(^{-1}\)),
- \( A \) is cross-sectional area of stream channel (m\(^2\)),
- \( D \) is dispersion coefficient (m\(^2\) s\(^{-1}\)),
- \( q_l \) is lateral volumetric inflow rate (per length) (m\(^3\) s\(^{-1}\) m\(^{-1}\)),
- \( C_l \) is solute concentration in the lateral inflow (mg L\(^{-1}\)),
- \( C_S \) is solute concentration in the storage zone (mg L\(^{-1}\)),
- \( A_S \) is cross-sectional area of the storage zone (m\(^2\)),
- \( \alpha \) is stream-storage exchange coefficient (s\(^{-1}\)),
- \( t \) is time (s), and
- \( x \) is distance (m).

Equations 1 and 2 define a quasi-two-dimensional solute-transport model. In equation 1, the first two terms on the right-hand side represent the advection and dispersion mechanisms, the third term represents lateral inflow, and the fourth term represents transfer to the storage zone. Equation 2 couples the storage zones to the stream and assumes mass transfer to be the only process active in the storage zones. Although the model defined by equations 1 and 2 is a simplification of the complex transport processes active in a stream, it has been demonstrated to reproduce the transient storage observed in small stream systems (see for example Bencala and Walters 1983, Bencala, 1984, Jackman and others, 1984, Bencala and others, 1990). Consequently, determining the “storage capacity” of a stream is a necessary first step in any study aimed at exploring more complex solute-stream interactions.

INVERSE MODEL FOR PARAMETER ESTIMATION

Most of the parameters that characterize transport in streams are difficult or impossible to measure directly and are instead estimated by fitting the model to solute concentration data obtained in stream tracer experiments. Obviously, manual calibration cannot guarantee the parameter estimates are in any sense optimal. Moreover, given some uncertainty in the concentration data and the error inherent in the conceptual/mathematical model, there is always a degree of uncertainty associated with the parameter estimates. Consequently the model-based predictions are also uncertain. A statistically based simulation-optimization inverse model has the advantage of identifying optimal parameter estimates and accounting for the uncertainty inherent in the parameter estimates and model predictions. The approach taken here is to couple solute-transport simulation with nonlinear least-squares regression analysis and first-order uncertainty analysis. The goal of the transport simulation - nonlinear regression inverse model is to identify the parameter values for the transport model that “best” reproduce the measured solute concentrations. First-order uncertainty analysis is then applied to quantify the reliability of the optimal parameter estimates.

In brief, the objective of a simulation-regression inverse model is to identify the parameter estimates that minimize the weighted sum of squared deviations between simulated and observed concentrations.
Parameter estimates that meet this objective are considered optimal for the given simulation model and concentration data. In order to apply the nonlinear regression methodology, it is necessary to postulate a statistical “model” for the random errors associated with the solute concentration data. These errors are defined as the difference between observed and simulated concentrations, and include measurement errors and errors resulting from the improper specification of the numerical simulation model. For this work, it is assumed the concentration errors are independent and normally distributed with mean zero, but it should be noted these assumptions are not required for application of the method. Under the assumption of independent and normally distributed errors, the nonlinear regression estimates are equivalent to maximum-likelihood estimates (Draper and Smith, 1981). A detailed discussion of nonlinear regression analysis for solute-transport parameter estimation is in Wagner and Gorelick (1986) and Wagner (1992).

An important component of parameter estimation is the analysis of parameter-estimate uncertainty. Asymptotically, the parameter estimates are normally distributed. As such, they are completely characterized by their mean and covariance. The parameter estimates serve as our estimate of the mean. The first-order approximation to the parameter estimate covariance matrix, $COV$, is (Yeh and Yoon, 1981, Carrera and Neuman, 1986)

$$COV = \sigma^2 (J^T J)^{-1}$$

where $\sigma^2$ is the variance of the random concentration errors and $J$ is the jacobian, the matrix of sensitivities of concentrations with respect to changes in the model parameters. In practice, $\sigma^2$ is unknown and is estimated based on the residual sum of squares (Draper and Smith, 1981). Together, the parameter estimates and the estimate covariance matrix serve to define statistically our knowledge of the parameters that determine transport. These statistical measures can be used to identify parameters that are poorly estimated, discriminate between competing model structures, assess the impact of parameter uncertainty on model predictions, and(or) evaluate the worth of data for experimental and monitoring network design.

**SOLUTE TRANSPORT PARAMETER ESTIMATION FOR PINAL CREEK**

For this study, the system of interest is Pinal Creek Basin, Arizona (fig. 1). Pinal Creek is a small meandering stream with low slope (approximately 1 percent) and a coarse sand and gravel bed. In November, 1992, a tracer experiment was conducted to study the transport of solutes in Pinal Creek (Harvey and others, 1996). A bromide tracer was introduced into the stream and solute concentrations were monitored at five stations along a 809-m reach (see inset, fig. 1), resulting in five comprehensive concentration histories. Using solute-concentration data collected during this experiment, we wish to analyze the transport parameters that characterize solute migration, attenuation, and redistribution.

This report, describes the transport between the injection site and sampling location 2, which is located 140 m downstream from the injection point. A Crank-Nicolson finite-difference approximation to the advective-dispersive and transient-storage transport model (equations 1 and 2) was developed to serve as the basis for the parameter-estimation study. The volumetric flow rate, $Q$, and the lateral inflow rate, $q_L$, were calculated from streamflow measurements at the injection site and sampling site 2. The background bromide concentration was assumed known on the

---

Figure 1. Site map for Pinal Creek Basin showing locations of surface and ground-water sampling stations for November, 1992 bromide tracer test.
basis of background concentrations measured at the injection point and sampling site 2. These background concentrations serve to define the solute concentration of the lateral inflow, $C_L$, and the initial concentrations in the stream and storage zones. Likewise, concentrations measured at sampling site 1 were used to define the concentration history at the upstream boundary of the simulation model. The resulting solute-transport simulation model has four unknown parameters - dispersion coefficient, $D$, stream cross-sectional area, $A$, storage-zone cross-sectional area, $A_s$, and stream-storage exchange coefficient, $a$. It should be noted that lateral mixing of the tracer was enhanced by narrowing the stream channel just below the injection point to less than ten centimeters wide. This ensured complete cross-channel mixing, which is an assumption of the one-dimensional solute transport model used here.

By use of the inverse model described earlier, the four unknown transport parameters were estimated on the basis of 21 in-stream concentration measurements at sampling site 2 (fig. 2). For comparison, the inverse model was also applied to estimate the dispersion coefficient and stream cross-sectional area assuming the transient-storage mechanism was inactive (that is, $a=0$). The optimal parameter estimates and their uncertainties are summarized in table 1. The optimal fitted concentration breakthrough curves at sampling location 2 are presented in figure 2. The parameter estimates and fitted breakthrough curves suggest that the transient-storage process is operative in Final Creek. In order to reproduce the measured concentration breakthrough accurately, the inverse model “activates” the transient-storage mechanism by

\[ D, m^2/s; A, m^2; A_s, m^2; a, s^{-1}; m^2/s, meters squared per second; m^2, meters squared; s^{-1}, inverse seconds \]

<table>
<thead>
<tr>
<th>Parameter Estimate with Transient Storage</th>
<th>Estimate Standard Deviation</th>
<th>Approximate 95 percent Confidence Limits</th>
</tr>
</thead>
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<tr>
<td>$D, m^2/s$</td>
<td>$8.83 \times 10^{-2}$</td>
<td>$1.60 \times 10^{-2}$</td>
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<td>$A, m^2$</td>
<td>$1.86 \times 10^{-2}$</td>
<td>$2.36 \times 10^{-4}$</td>
</tr>
<tr>
<td>$A_s, m^2$</td>
<td>$3.12 \times 10^{-3}$</td>
<td>$2.64 \times 10^{-4}$</td>
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<td>$a, s^{-1}$</td>
<td>$6.70 \times 10^{-4}$</td>
<td>$1.03 \times 10^{-4}$</td>
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</table>

<table>
<thead>
<tr>
<th>Parameter Estimate without Transient Storage</th>
<th>Estimate Standard Deviation</th>
<th>Approximate 95 percent Confidence Limits</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D, m^2/s$</td>
<td>$7.27 \times 10^{-2}$</td>
<td>$3.40 \times 10^{-2}$</td>
</tr>
<tr>
<td>$A, m^2$</td>
<td>$1.95 \times 10^{-2}$</td>
<td>$4.13 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

Figure 2. Optimal fitted concentration breakthrough curves for transport with transient storage (solid line) and without transient storage (dashed line). Circles represent concentration data used in the parameter estimation study.

Table 1. Results of solute transport parameter estimation for Pinal Creek tracer study
selecting a nonzero value for the stream-storage exchange coefficient along with the “best fit” storage-zone cross-sectional area. Furthermore, the uncertainty analysis indicates that these parameter estimates are reliable. The parameter-estimate standard deviations, as a percentage of the estimates, range from approximately 1 percent for the stream cross-sectional area to approximately 18 percent for the dispersion coefficient. The result is a fitted concentration breakthrough that is an excellent simulation of the observed data. Conversely, the advective-dispersive equation alone cannot adequately reproduce the transient storage effect, which is obvious at the “shoulder” of the breakthrough curve where the solute concentrations rise less rapidly than those predicted by the simple advective-dispersive model. The effect of this “lack-of-model-fit” is evident in the parameter-estimate standard deviations, which have increased to approximately 2 percent of the stream cross-sectional area estimate and approximately 46 percent of the dispersion coefficient estimate.

The optimal parameter estimates and fitted concentration histories indicate the transient-storage mechanism is an important transport process in Pinal Creek. The validity of the model rests on the assumption that the storage parameter estimates are physically realistic. By comparing the estimates with those in other studies (Bencala and Walters, 1983, Bencala, 1984, Bencala and others, 1990), it is evident that the values are at least plausible. Both the exchange coefficient and storage cross-sectional area estimates fall within the range of values in those studies.

SENSITIVITY ANALYSIS AND SAMPLING NETWORK DESIGN

Sampling-network design is, like parameter estimation, an optimization problem. The goal is to identify the sampling strategy (timing, location and number of measurements) that maximizes the information content of the data collected. The definition of “information content” depends on the sampling objective(s), but, in the case of parameter estimation, a logical goal would be to identify a sampling strategy that will yield reliable parameter estimates. In studies of solute-transport parameter estimation, the concentration sensitivity (partial derivative of concentration with respect to changes in a parameter value) plays an important role in defining the worth of data for parameter estimation (see Knopman and Voss, 1987). The concentration sensitivities for the parameter estimation problem presented in the previous section are shown in figure 3.

Figure 3. Concentration sensitivity plots for (a) dispersion coefficient (b) stream cross-sectional area (c) storage-zone cross-sectional area and (d) stream-storage exchange coefficient, sampling site 2 in Pinal Creek, Ariz. Solid line represents concentration sensitivity. Dashed line represents optimal fitted concentration breakthrough. Circles denote concentration sensitivities for the data used in the parameter estimation study.
Shown are the sensitivities of simulated streamwater concentrations to dispersion ($\partial C/\partial D$, fig. 3a), stream cross-sectional area ($\partial C/\partial A$, fig. 3b), storage-zone cross-sectional area ($\partial C/\partial A_s$, fig. 3c) and stream-storage exchange coefficient ($\partial C/\partial \alpha_s$, fig. 3d). Superimposed on the sensitivity plots is the concentration breakthrough curve simulated using the optimal parameter estimates. Highlighted by circles are the concentration sensitivities for the data used in the parameter estimation study.

From inspection of equation 3 and the concentration sensitivity plots in figure 3, the following principles of sampling network design emerge: (1) Information about a parameter is most efficiently gained by sampling at points with high sensitivity to the parameter. Concentration sensitivities define the elements of the jacobian matrix in equation 3. By maximizing the absolute sensitivities, we maximize the elements of the matrix $J^TJ$, which is inversely proportional to the parameter estimate covariance (see eq. 3). (2) Data that minimize the uncertainty of one parameter may not minimize the uncertainty of other parameters. Inspection of figure 3c indicates the maximum sensitivity for storage-zone cross sectional area occurs at 10.6 hours. Sensitivities for the other parameters, however, are far from their maximum absolute values at this time. (3) The concentration history is sensitive to the parameters over specific, narrow time spans. The maximum sensitivity to the dispersion coefficient occurs at the first arrival of solutes. For the stream cross-sectional area, the maximum sensitivity occurs at the mid-point of the rise of the breakthrough curve. For the storage-zone cross-sectional area and stream-storage exchange coefficient, the maximum sensitivities occur at the tail and shoulder, respectively, of the breakthrough curve. (4) The sensitivity plots presented in figure 3 represent local derivatives of concentration with respect to these parameters. The range of parameter values for which these sensitivities are valid will depend on the degree of nonlinearity of the governing transport model.

Observation (4) above suggests that the design of an "optimal" sampling network will be based on assumptions regarding the governing transport model and the parameter values that, paradoxically, the sampling network is being designed to estimate. Two steps can be taken to overcome this difficulty. When possible, data collection should be approached as a multi-stage process in which, after each sampling stage, the parameter estimates are refined and the sampling network is revised or supplemented. When multi-stage sampling is not possible, such as in the case of a stream-tracer study, robust sampling strategies should be identified to ensure the parameter estimates are reliable for the range of possible parameter values.

**SUMMARY**

Solute-transport simulation is a valuable tool for investigating the effect of contamination on water quality. A key step in the development of solute-transport simulation models is the estimation of parameters that characterize solute migration, attenuation, and redistribution. A technique for estimating the parameters that characterize the transport of contaminants has been demonstrated using data from an injection experiment at Pinal Creek, Arizona. The methodology, which couples solute-transport simulation with nonlinear least-squares regression and first-order uncertainty analysis, was applied to analyze parameters for a one-dimensional solute-transport model with advection, dispersion, lateral inflow, and transient storage. Results of the analysis suggest that accurate simulation of transport in Pinal Creek requires modeling both the advective-dispersive and transient-storage processes. Conversely, parameter estimation for the simple advective-dispersive model indicates that advection and dispersion alone cannot adequately reproduce the effects of transient storage. Current work focuses on extending the analysis presented here to study the trends in parameter estimates along an 809-m reach of Pinal Creek.

A logical goal of sampling-network design for a tracer experiment is to identify a sampling strategy that will yield reliable parameter estimates. We demonstrated how the analysis of concentration sensitivities to the unknown parameters of the transport model can be used to evaluate the value of data for parameter estimation. Although this example did not address some important issues of parameter estimation (for example, parameter non-identifiability), it nonetheless demonstrates the quantitative relation between concentration sensitivities, estimation uncertainty, and sampling-network design.
REFERENCES CITED


Alteration of Alluvium by Acidic Ground Water Resulting from Copper Mining at Pinal Creek, Arizona

By Carol J. Lind\textsuperscript{1} and Kenneth G. Stollenwerk\textsuperscript{2}

Abstract

A composited core of alluvium collected downgradient from a metal-rich, acidic ground-water plume was eluted with ground water from the plume in a column experiment.

The major minerals present in the alluvium before and after elution were identified, and resulting changes in mineral content and in ground-water composition were correlated. Of the 12 identified minerals, the ground water dissolved two carbonate minerals and pyrolusite and partially dissolved the feldspars.

INTRODUCTION

More than 100 years of copper (Cu) mining has created a metal-rich, acidic ground-water plume in the Pinal Creek, Arizona, drainage basin (Envirologic Systems, Inc., 1983). The plume is formed as the ground water moves through the alluvium below the intermittent reach of Pinal Creek and mixes with water infiltrating from the Cu-mining area. This contaminated ground water reacts with the alluvium, dissolving some minerals and depositing others. The reacted ground water, moving downgradient from the mining area towards the creek mouth, contributes to the streamflow in the perennial reach of Pinal Creek (fig. 1).

This paper defines, by means of X-ray-diffraction (XRD) analysis, the major minerals present before and after contact with the metal-rich, acidic ground water and correlates changes in mineralogy with changes in ground-water composition. This work is the first step in the study of the alluvium composition before and after exposure to this contaminated water. The ultimate study objective is to define the location and, if possible, oxidation states of trace metals, especially iron (Fe) and manganese (Mn), within the mineral structures of the major minerals present and at the surfaces of these minerals.

MINERALOGIC BACKGROUND

The Pinal Creek shallow alluvium consists of sand, gravel, and fragments of mineralized schist and granite porphyry. The shallow alluvium is surrounded by basin fill that consists of interfingering lenticular beds of gravel, sand, and silt, many of them firmly indurated by calcareous cement. The sand consists mostly of dacitic and decomposed diabase, but grains of other rock types also are present. Most of the fragments are well rounded (apparently from being transported considerable distances) and consist mostly of rocks of the Apache Group and Troy Quartzite: other rock materials consist of limestone, dacite and diabase (Ransome, 1903; and Peterson, 1962).

MATERIALS AND METHODS

The studied alluvium was a composite of five samples of the <2-mm (millimeter) core material from well 600 (fig. 1). Well 600 is in the perennial reach of the creek, downgradient from the acidic, metal-rich, ground-water plume. The depth intervals, in feet, from which the five composited alluvial samples were collected are 11 to 13, 16 to 17, 20 to 23, 26 to 28, and 36 to 39.5. The samples contained 0.26 to 0.67 percent carbonate (as calcite) and the composited sample contained 0.41 percent carbonate. The ground water to be eluted was sampled from well 101, which is directly in the path of drainage from Cu-mining activities and adjacent to well 100 (fig. 1).
Figure 1. Map showing the Pinal Creek drainage basin, the mines, tailings, and well sites (adapted from Eychaner (1991), p. 440, fig. 1).

A column, 30 cm (centimeters) long by 2.5 cm inside diameter, was packed with the composited alluvium, flushed with nitrogen, eluted with deionized water (also flushed with nitrogen), and then eluted with the ground water which had a pH of 3.86. A total of 13.6 pore volumes were required to change the groundwater effluent pH from 7.6 to 4.6. A pH of 4.6 represents pH of water well within the advancing ground-water plume in 1990 (Lind and Hem, 1993). Table 1 lists the original ground water and the final effluent aliquot compositions.

The measurement of magnetic susceptibility and grain size distribution in the alluvium before and after exposure to the ground water (original alluvium and
eluted alluvium, respectively) provided a general knowledge of alluvial composition and its alteration by the contaminated ground water. Also, the concentration of certain minerals by segregation according to magnetic susceptibility facilitated their identification by XRD. The original and eluted alluvium were each separated by size into six fractions by dry sieving through an acid-washed, nonmetallic sieve (table 2). The more magnetic particles (MMP) were removed from each of these 12 fractions with a hand-held horseshoe magnet covered with a disposable glove. The alluvial particles segregated by hand magnet are categorized as nonmagnetic (NMP, not removed by contact with magnet poles), magnetic (MP, removed by contact with magnet poles), strongly magnetic (SMP, removed by waving magnet slightly above the sediment), and, for the 0.25- to 2-mm size fraction, very strongly magnetic (VSMP, removed by waving magnet about 1 cm above the alluvium). The NMP 150- to 250-(j,m size fractions were further segregated with a Frantz magnetic separator according to their slight susceptibility to a magnetic field.

Table 1. Composition of groundwater from well-101 and of final aliquot of eluted water

<table>
<thead>
<tr>
<th>Property or constituent</th>
<th>Units of measurement</th>
<th>Value or concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxidation-reduction potential</td>
<td>mV</td>
<td>430</td>
</tr>
<tr>
<td>Specific Conductance</td>
<td>μS/cm @25o</td>
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</tr>
<tr>
<td>Dissolved Oxygen</td>
<td>mg/L</td>
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</tr>
<tr>
<td>pH (field)</td>
<td>std. units</td>
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<tr>
<td>(laboratory)</td>
<td></td>
<td>3.86 4.63</td>
</tr>
<tr>
<td>Total hardness</td>
<td>mg/L as CaCO3</td>
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</tr>
<tr>
<td>Major dissolved ions1</td>
<td>mg/L</td>
<td></td>
</tr>
<tr>
<td>Aluminum</td>
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<td>~19.</td>
</tr>
<tr>
<td>Calcium</td>
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<td>872.</td>
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<tr>
<td>Copper</td>
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<tr>
<td>Iron</td>
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<td>(710.)</td>
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<td>Magnesium</td>
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<tr>
<td>Manganese</td>
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<td>Sulfate</td>
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</tbody>
</table>

1Besides the metals listed, one or more mg/L of Co, Ni, Sr, and Zn were in the groundwater before elution. Only Co and Zn were measured in the eluant and the analysis precision did not warrant listing their concentrations.

With the exception of the 20- to 38-μm eluted alluvium and the 63- to 75-μm MMP of the original and the eluted alluvium, a representative aliquot of the each magnetically segregated part (including those separated by the Frantz magnetic separator) of every size fraction was removed by splitting, finely ground, and then examined by XRD. The results were analyzed using the Nicolet computer program and the major minerals were identified. The gain or loss of a mineral phase caused by elution of the ground water was estimated by comparison of XRD patterns for the original alluvium with those for the eluted alluvium. This gain or loss in a magnetically segregated part of a size fraction was based on the change in XRD relative intensities (RI), relative peak heights, for the mineral in question compared with the XRD RI of the predominant mineral for that segregated part. The predominant minerals were magnetite for the most magnetic part and quartz for the lesser magnetic parts of each size-fraction. The XRD RI for a given mineral are the ratios of counts-per-second of the secondary peaks divided by counts-per-second of the strongest peak multiplied by 100. Small concentrations changes for the most predominant mineral for a segregated part would not be observed using this method.

RESULTS AND DISCUSSION

General Observations

Much of the alluvium had a grain size of 0.25 to 2 mm and the weight-percent of each size fraction (relative to the total sample) decreased with decreasing grain size. The 11 percent decrease in the 0.25- to 2-mm size fraction and the 11 percent increase in the 38- to 250-μm size fractions after elution indicates that the acidic ground water dissolved and (or) disaggregated and reduced the size of the alluvial particles (table 2). In addition to dissolution of the alluvium by the ground water, the loss of some of the 20- to 38-μm size fraction could be caused by particles being washed out by the eluant.

In the alluvium, MMP and NMP must be dissolving simultaneously because in all of the <250- to the >38-μm size fractions, the weight-percent of NMP was about the same after elution as before and there was only a one percent decrease in the 0.25- to 2-mm size fraction, probably not experimentally significant (table 2).
Table 2. Distribution of particles in alluvium by size and magnetic susceptibility

[NMP, nonmagnetic part = not removed when in contact with the poles of a magnet, a horseshoe hand magnet covered by a disposable glove; MP, magnetic part = removed by contact with magnet poles; SMP, strongly magnetic part = removed by waving magnet slightly above the alluvium; VSMP, very strongly magnetic part = removed by waving magnet about 1 centimeter above alluvium; \( \mu \text{m} \), micrometer; \%, weight-percent; xx, original alluvium; and [xx], eluted alluvium.]

<table>
<thead>
<tr>
<th>Size (( \mu \text{m} ))</th>
<th>NMP (% of size fraction)</th>
<th>NMP (% of the entire sample)</th>
<th>MP</th>
<th>SMP</th>
<th>VSMP</th>
<th>Total (% of the entire sample)</th>
</tr>
</thead>
<tbody>
<tr>
<td>250-2000</td>
<td>87.88</td>
<td>57.60</td>
<td>5.19</td>
<td>2.29</td>
<td>0.46</td>
<td>65.54</td>
</tr>
<tr>
<td>[86.90]</td>
<td></td>
<td>[47.29]</td>
<td>[6.48]</td>
<td>[3.7]</td>
<td>[1.28]</td>
<td>[54.42]</td>
</tr>
<tr>
<td>150-250</td>
<td>92.52</td>
<td>18.15</td>
<td>1.11</td>
<td>.36</td>
<td>.29</td>
<td>19.62</td>
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<tr>
<td>[92.95]</td>
<td></td>
<td>[22.77]</td>
<td>[1.20]</td>
<td>[.52]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>75-150</td>
<td>91.78</td>
<td>8.78</td>
<td>.49</td>
<td></td>
<td></td>
<td>2.90</td>
</tr>
<tr>
<td>[91.87]</td>
<td></td>
<td>[13.41]</td>
<td>[.74]</td>
<td>[.45]</td>
<td></td>
<td>[14.60]</td>
</tr>
<tr>
<td>63-75</td>
<td>96.16</td>
<td>1.92</td>
<td>.04</td>
<td>.04</td>
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<td>2.00</td>
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<tr>
<td>[96.11]</td>
<td></td>
<td>[3.63]</td>
<td>[.06]</td>
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<tr>
<td>38-63</td>
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<tr>
<td>[99.03]</td>
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<td>[2.64]</td>
<td>[.03]</td>
<td></td>
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<td>[2.67]</td>
</tr>
<tr>
<td>20-38</td>
<td>.26</td>
<td>.26</td>
<td>[.03]</td>
<td></td>
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<td>100.00</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[0.03]</td>
<td>99.99</td>
</tr>
</tbody>
</table>
Figure 2. The X-ray-diffraction evidence of alluvial minerals and of mineralogical changes caused by ground-water elution. The patterns of 150- to 250-micrometer size fractions, segregated with a horseshoe hand magnet covered by a disposable glove, show (A) magnetite predominance, pyrolsute dissolution, and some hematite loss; (B) mineral diversity and feldspar partial dissolution; and (C) a carbonate dissolution (carbonate major peak is between the thick bars shown for dolomite and huntite.)
The XRD did not detect minor minerals or newly precipitated minerals in the 150- to 250-μm size fraction separated by the Frantz magnetic separator. Correlation of the precipitation model of Bigham and others (1992) with ground-water composition suggests the possible presence of ferrihydrite (\(-\text{Fe}_5\text{HO}_8\cdot4\text{H}_2\text{O}\)) in the original alluvium and schwertmannite (\(-\text{Fe}_8\text{O}_8\cdot(\text{OH})_6\cdot\text{SO}_4\)) in the eluted alluvium, but XRD did not detect these minerals.

**Mineralogical Changes Correlated With Water Chemistry**

At the time the elution was stopped, the ground-water/alluvium interaction was removing Al, Cu, and Fe from the ground water and Ca, Mg, and Mn from the alluvium. Many identified minerals in the alluvium contained Al and (or) Fe, but after elution, no new Al, Cu, and (or) Fe solids were discernable by XRD. Quite possibly, the percentage of new, well-crystallized minerals was too low to be seen by XRD or, more likely, much of the Al and Fe was precipitating as finely divided amorphous solids that could also remove Cu. The observed increase in Ca, Mg, and Mn concentrations in the eluant could be explained by dissolution of feldspars, carbonates, and perhaps tremolite to release Ca; carbonates and possibly tremolite to release Mg; and pyrolusite and carbonate to release Mn. The data did not permit conclusions concerning distribution of the trace metals Co, Cd, Ni, Sr, and Zn (table 1).

**SUMMARY**

A composited core of alluvium collected downgradient from a metal-rich, acidic ground-water plume was eluted with the metal-rich, acidic ground water in a column experiment. Alluvium from before and after the elution was segregated by size and magnetic susceptibility and then examined by XRD. The alteration of minerals by the elution was estimated by comparison of their XRD relative peak intensities with those of the major mineral present in the respective magnetically segregated part of each grain-size fraction.

Twelve minerals were identified. The dissolution of the carbonates (dolomitic in structure) pyrolusite, and perhaps tremolite, and the partial dissolution of feldspars could explain increases in Ca, Mg, and Mn concentrations in the final ground-water eluant; precipitation, exchange and (or) surface reactions could explain decreases in Al, Cu, and Fe concentrations in this water. The chemical formulas of many of the 12 initially identified minerals contain Fe or Mn. No new Al, Cu, or Fe minerals were identified after elution.

**SELECTED REFERENCES**


Chemical Processes in Manganese Oxide and Carbonate Precipitation in Pinal Creek, Arizona

By John D. Hem and Carol J. Lind

Abstract

Two water samples from well 503 near the head of the perennial reach of Pinal Creek and one sample of surface flow at the Setka Ranch crossing about 2 kilometers downstream from the well were used as the manganese-bearing solution in automated pH-stat titration with a 0.10 molar NaOH solution while bubbling CO₂-free air into the mixture. The three samples had manganese concentrations ranging from 63 to 94 mg/L and dissolved solids concentrations ranging from 3,500 to 3,570 mg/L, mostly consisting of Ca and SO₄. The ground-water samples initially were about 5 x 10⁻³ molar in undissociated dissolved CO₂ and had pH's near 6. The creek water had a pH near 7 and a CO₂ concentration smaller than 10⁻³ molar. Titration of one ground-water sample done without removing the dissolved CO₂ produced a mixture of hausmannite (Mn₃O₄) and kutnahorite (CaMn(CO₃)₂). The other two samples were treated to decrease the dissolved CO₂ species before titration. One of these samples yielded mainly hausmannite during titration that altered on aging to manganite (MnOOH). The other sample yielded a mixture of oxides that altered on aging to a mixed Ca + Mn species similar to todorokite ((Mn²⁺, Ca) Mn⁴⁺₅ O₁₁ • 4H₂O) in which most of the manganese is in the 4⁺ oxidation state. X-ray-diffraction studies of precipitates from Pinal Creek identified kutnahorite in carbonate cemented crusts near the head of perennial flow. The mixed Ca + Mn⁴⁺ oxides also were identified near the head of perennial flow and in black precipitates farther downstream.

INTRODUCTION

The ground water in alluvium underlying Pinal Creek has been contaminated by seepage of waste solutions produced in copper mining and ore treatment that were impounded by piles of mill tailings in the tributary basin of Miami Wash. In February 1988 the impounded water had a pH of 2.7. Dissolved concentrations at that time included: sulfate, 20,000 mg/L; iron, 5,970 mg/L; aluminum, 850 mg/L; copper, 210 mg/L; manganese, 100 mg/L; zinc, 32 mg/L; and cobalt, 20 mg/L (Brown, 1990).

The contaminated water has escaped from the impoundment as underflow in the alluvium that underlies the tailings piles and moved downstream beneath Miami Wash into the alluvial aquifer that underlies the valley of Pinal Creek (fig. 1). As it moved downstream the acidity in this seepage plume was neutralized by reactions with solids (mainly CaCO₃) in the alluvium, and most metals are removed. The neutralized seepage attains a pH between about 5.5 and 6.5. About 8 km downstream from the confluence of Pinal Creek and Miami Wash, the valley narrows, forcing groundwater to the surface and creating perennial flow in the creek (fig. 1). Predominant solutes in the neutralized water at this point are calcium and sulfate at concentrations near saturation with respect to gypsum. Chemical analyses of surface flow at the Setka Ranch crossing, near the head of flow, are given by Brown (1990). The analyses of surface flow in the creek and of adjacent shallow ground water show that in recent years dissolved manganese concentrations have commonly ranged from 50 to 100 mg/L. Black manganese oxide crusts occur on rock and sand surfaces in the creek bed.

Figure 1. Location map of study area showing sampling sites. (Modified from Brown, 1990, fig. 1).
This paper presents results obtained when manganese was precipitated from samples of contaminated water from the Pinal Creek site under carefully controlled laboratory oxidation conditions. Precipitates obtained from the contaminated water are compared with the precipitates that occur in the Pinal Creek system and with those obtained in earlier research.

**EXPERIMENTAL**

Previous laboratory studies have defined effects of temperature and pH on rates of oxidation and the form of oxide produced. The latter also is affected by the predominant anion in the solution (Hem, 1978, 1980, 1981; Hem and Lind, 1983). The oxidation occurs preferentially at solid mineral surfaces, especially those of preexisting manganese oxide.

**Table 1. Chemical composition of water from Well 503, near Pinal Creek, 16 km. northwest of Globe, Arizona and from surface flow in Pinal Creek at Setka Ranch, 18 km northwest of Globe, Arizona**

[Concentrations of major constituents are milligrams per liter, except as noted]

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica (SiO₂)</td>
<td>69</td>
<td>67</td>
<td>60</td>
</tr>
<tr>
<td>Manganese (Mn)</td>
<td>86</td>
<td>94</td>
<td>63</td>
</tr>
<tr>
<td>Calcium (Ca)</td>
<td>690</td>
<td>655</td>
<td>680</td>
</tr>
<tr>
<td>Magnesium (Mg)</td>
<td>140</td>
<td>170</td>
<td>150</td>
</tr>
<tr>
<td>Sodium (Na)</td>
<td>91</td>
<td>113</td>
<td>91</td>
</tr>
<tr>
<td>Undissociated</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diss. C0₂ Calc. (H₂C0₃)</td>
<td>380¹</td>
<td>320¹</td>
<td>46¹</td>
</tr>
<tr>
<td>Bicarbonate (HC0₃)</td>
<td>113²</td>
<td>57²</td>
<td>110²</td>
</tr>
<tr>
<td>Sulfate (SO₄)</td>
<td>2,300</td>
<td>2,250</td>
<td>2,400</td>
</tr>
<tr>
<td>Chloride (Cl)</td>
<td>120</td>
<td>124</td>
<td>120</td>
</tr>
<tr>
<td>Dissolved solids (Sum)</td>
<td>3,550</td>
<td>3,500</td>
<td>3,570</td>
</tr>
<tr>
<td>Specific Conductance (µS/cm, 25°C)</td>
<td>3,800</td>
<td>3,610</td>
<td>3,880</td>
</tr>
<tr>
<td>pH (field)</td>
<td>5.94</td>
<td>5.72</td>
<td>6.80</td>
</tr>
<tr>
<td>pH (lab)</td>
<td>6.44</td>
<td>8.76⁵</td>
<td>4.93⁴</td>
</tr>
<tr>
<td>Dissolved Oxygen (O₂)</td>
<td>6.44</td>
<td>&lt;1</td>
<td>6.7</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>18.0</td>
<td>18.0</td>
<td>18.5</td>
</tr>
</tbody>
</table>

Source of Data: Brown (1990)
Analyst: J.D. Hem

Brown (1990)

¹ Based on field measurements of HC0₃⁻ and pH.
² Determined in field at time of sampling.
³ pH after treatment to lower H₂C0₃⁻.
⁴ pH after treatment to decrease HC0₃⁻.

Two samples of ground water from observation well 503 (fig. 1) collected in 1989 and 1991, and a sample of water from Pinal Creek at the nearby Setka Ranch crossing collected in 1989, were used in the laboratory experiments. Analyses of these samples are given in table 1. The manganese was oxidized by a continuous titration technique, in which manganese-bearing solution was added to a temperature-controlled reaction vessel at a constant slow rate by an autoburet. The pH was maintained at a prescribed constant value by addition of a standard base (0.10 molar NaOH) from a pH-stat, while air freed from CO₂ was bubbled into the stirred reacting solution. A steady state was reached after a brief induction period and the composition and mineralogy of the precipitate and solution composition were determined by taking samples from the reaction vessel. After titration was stopped the solution with its precipitate was allowed to age at room temperature. Additional samples of the solution and precipitate were analyzed during aging.

The first precipitation experiment (503-1) used water from well 503, which is screened at the depth interval of 23.4 to 24.1 m. When the sample was collected, its pH and bicarbonate alkalinity were determined. From these data the concentration of undissociated carbon dioxide (CO₂) given in table 1 was calculated. Some of the CO₂ had escaped by the time the laboratory pH measurement was made, but the amount present was still substantially greater than 100 mg/L (as H₂CO₃). For the other two experiments, PC-1 and 503-2, the water samples were pretreated to decrease their dissolved CO₂-species content. Sample PC-1, water from Pinal Creek at Setka Ranch, was acidified to pH 4.93 and bubbled with CO₂-free air, which removed CO₂ and most of the HCO₃⁻ before the titration began. The third titration used a later (Nov. 22, 1991) sample from well 503, which was pretreated by bubbling into it CO₂-free air, without prior acidification. This treatment did not decrease the HCO₃⁻ concentration, but the final pH was 8.76.

The experimental conditions in 503-1 were intended to simulate conditions in ground water immediately after coming into contact with air, as in seepage just as it enters Pinal Creek, or at the surface of a rising water table. Under these conditions both oxygen and CO₂ would be in solution. The second and third titrations, PC-1 and 503-2, were intended to simulate conditions that might be attained after aeration in Pinal Creek had removed most of the dissolved CO₂. The pH of the water samples was held at 9.00 in the first few hours of each titration and was
lowered to 8.75 for the rest of the titration. At the gaging and sampling station at Inspiration Dam, about 8 km downstream from well 503, data of Brown (1990) and Longsworth and Taylor (1992) show that the pH is generally about 8.0 ± 0.2 units. The higher experimental pH increases the rate of oxidation, but previous experiments have shown the form of oxide is not affected significantly.

The oxidation state of manganese in the precipitates was determined by a redox titration technique (Hem, 1980). The specific forms of manganese oxide that were present were determined by X-ray and electron diffraction. Mineralogic identification of precipitates recovered from Final Creek were given earlier by Lind and Hem (1993).

RESULTS AND DISCUSSION

Activities of solutes in experimental solutions during redox titration and aging are given in table 2, as are values for the oxidation state of precipitated manganese. During titration experiment 503-1 the measured oxidation number of precipitated manganese was consistently below 2.50. The lowest oxidation number for manganese oxides produced in our earlier work where dissolved HCC>3~ was absent was near 2.67, the value to be expected for hausmannite (Mn3O4). The lower values seen in this titration indicate the presence of other divalent manganese species in the precipitate. The X-ray-diffraction data indicated the presence of kutnahorite, a mineral with a dolomite crystal structure, in pure form having the formula CaMn(CO3)2. Some magnesium can substitute for manganese in natural kutnahorite. This mineral was also found in streambed precipitates in Final Creek by Lind and Hem (1993). During aging, the oxidation number of the precipitated manganese increased to 2.65. Hausmannite was in the precipitate formed during titration, and the kutnahorite probably was converted to oxide during aging.

In titration experiment PC-1, the oxidation number of precipitated manganese was 2.66 or greater during titration, indicating that carbonates probably were absent. The measured value rose to 2.99 during aging. The initial precipitate appeared to be hausmannite, which altered during aging to the Mn3+ oxide, manganite. This alteration is similar to that seen in earlier titration experiments in simpler solutions (Hem and Lind, 1983). In the first few hours of the titration experiment 503-2, the air bubbler was not operated and a small amount of precipitate in which the manganese oxidation number was below 2.5 was formed. During aeration the oxidation number approached 3.0. During aging the manganese oxidation number increased, finally reaching 3.62 after 112 days. In this sample, the X-ray-diffraction data indicate the presence of the mixed Ca and Mn4+ oxides todorokite ((Mn2+, Ca)Mn4+5 O11 • 4H2O) and takanelite ((Mn2+, Ca)Mn4+4 O9 • 3H2O). These oxides also were identified by Lind and Hem (1993) in black cemented precipitates collected from Final Creek at the streamflow gaging station at Inspiration Dam. These precipitates had been in place for at least a year.

A thermodynamic evaluation of the feasibility of various precipitation and alteration reactions was made by calculating affinities of reaction (Δ) for the precipitation of oxide and carbonate species, in the experimental solutions 503-1, PC-1 and 503-2. The affinity of reaction is calculated from the relation

\[ \Delta = -2.303 \text{ RT} \left( \log Q - \log K \right) \]

where R is the gas constant; T is temperature on the kelvin scale; Q is the activity quotient calculated by entering observed reactant and product activities in the mass-law equation for the reaction considered, written as producing a precipitate; and K is the equilibrium constant for that reaction. Positive values for Δ indicate the reaction is favored to proceed to the right, as written.

Calculated values for Δ (table 3) for the precipitation of kutnahorite are positive during all the titrations, as are those for hausmannite and manganite. Kinetics appear to favor the oxidation reactions. The reaction affinities for the mixed Ca + Mn4+ oxides could not be calculated because standard free energies of formation for these species are not known.

CONCLUSIONS

Substantial amounts of dissolved undissociated CO2 species are present in the contaminated groundwater and in the perennial-flow reach of Pinal Creek. Most of the CO2 escapes as a gas when the water reaches the creek. The most favorable condition for carbonate precipitation probably occurs near the streambed surface where ground water seeps into the creek.
Table 2. Ion activities and manganese oxidation states during titration and aging

<table>
<thead>
<tr>
<th>Experiment and sample number</th>
<th>Titration time, hours</th>
<th>Aging time, days</th>
<th>Log of activity, mol/L</th>
<th>Mn oxidation number</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Ca$^{2+}$</td>
<td>Mn$^{2+}$</td>
</tr>
<tr>
<td>503-1-G</td>
<td>48</td>
<td>0</td>
<td>-2.36</td>
<td>-3.90</td>
</tr>
<tr>
<td>H</td>
<td>3</td>
<td></td>
<td>-2.38</td>
<td>-4.20</td>
</tr>
<tr>
<td>I</td>
<td>83</td>
<td></td>
<td>-2.31</td>
<td>-3.56</td>
</tr>
<tr>
<td>PC-1-E</td>
<td>39</td>
<td>0</td>
<td>-2.31</td>
<td>-4.24</td>
</tr>
<tr>
<td>F</td>
<td>132</td>
<td></td>
<td>-</td>
<td>-6.34</td>
</tr>
<tr>
<td>503-2-H</td>
<td>22</td>
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<td>-4.24</td>
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<tr>
<td>I</td>
<td>25</td>
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<td>-4.45</td>
<td>-7.68</td>
</tr>
<tr>
<td>J</td>
<td>112</td>
<td></td>
<td>-4.57</td>
<td>-7.26</td>
</tr>
</tbody>
</table>

Table 3. Thermodynamic feasibility of chemical reactions for precipitation or alteration of solids

<table>
<thead>
<tr>
<th>Experiment and sample number</th>
<th>Titration time, hours</th>
<th>Aging time, days</th>
<th>Mn Oxidation number</th>
<th>Affinity of reaction, kcal</th>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Δ1</td>
</tr>
<tr>
<td>503-1-G</td>
<td>48</td>
<td>0</td>
<td>2.44</td>
<td>5.65</td>
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<td>H</td>
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<td>4.26</td>
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<td>I</td>
<td>83</td>
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<td>-</td>
</tr>
<tr>
<td>PC-1-E</td>
<td>39</td>
<td>0</td>
<td>2.69</td>
<td>2.31</td>
</tr>
<tr>
<td>F</td>
<td>132</td>
<td></td>
<td>2.99</td>
<td>-</td>
</tr>
<tr>
<td>503-2-H</td>
<td>22</td>
<td>0</td>
<td>2.87</td>
<td>3.15</td>
</tr>
<tr>
<td>I</td>
<td>25</td>
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<td>3.21</td>
<td>-</td>
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<tr>
<td>J</td>
<td>112</td>
<td></td>
<td>3.62</td>
<td>-</td>
</tr>
</tbody>
</table>

As the pH increases downstream, and dissolved oxygen becomes more available, the rate of manganese oxidation increases. The high concentration of calcium in the water probably favors the mixed Ca$^{2+}$Mn$^{4+}$ oxide species identified in downstream deposits and in aged precipitates from titration experiment 503-2. Comparison of experimental results with observed manganese precipitation in Pinal Creek demonstrates that a better understanding can be achieved by applying tested chemical principles.

REFERENCES


Experimental Studies of Trace-Metal Partitioning in Perennial Reaches of Pinal Creek, Arizona

By Christopher C. Fuller

Abstract

Development of solute transport models to predict the fate of metal contaminants in Pinal Creek will require quantification of the reactions controlling metal partitioning. Manganese oxides are thought to control dissolved trace-metal concentrations in the perennial flow of the creek. However, these processes are not adequately characterized. Laboratory experiments under geochemical conditions relevant to Pinal Creek using field-derived materials are proposed to evaluate metal uptake by coprecipitation with manganese during oxidation and precipitation of manganese oxides and by adsorption onto absorbent phases present in the streambed sediments. The reversibility of the metal sorption by these processes also will be investigated.

INTRODUCTION

The increase in dissolved manganese (Mn), nickel (Ni) and cobalt (Co) in the perennial flow of Pinal Creek (fig. 1) from 1985 to present (Eychaner, 1991a) has indicated the need to develop predictive models that describe the transport of these metals. Using simple conservative and reactive mixing models, Eychaner (1991b) suggested that the downstream decrease in dissolved Mn results largely from Mn oxidation and precipitation of Mn oxides. Downstream decreases in surface-water concentrations of Ni, Co, and other trace metals in March 1990, also were observed (Faires and Eychaner, 1991). Because of their abundance, Mn-oxide phases are believed to be largely responsible for trace-metal partitioning by sediments (Lind and Anderson, 1992). However, trace-metal partitioning processes in Pinal Creek have not been sufficiently quantified for incorporation into reactive transport models. A more detailed description of the study site is given by Brown and Harvey (1996).

Development of solute transport models to adequately predict the fate of metals in Pinal Creek will require a quantitative description of trace-metal partitioning processes under geochemical conditions relevant to the perennial-flow regime of the stream. This will be of particular importance for simulating the potential inflow of an acidic ground-water plume, which contains high concentrations of dissolved copper (Cu), iron (Fe) and other metals (Eychaner, 1991a). The objective of this work is to investigate trace-metal partitioning processes in Pinal Creek by using field samples in laboratory experiments. The results will be used to provide the appropriate trace-metal partitioning and rate coefficients for incorporation into reactive transport models in the perennial reaches of Pinal Creek (Harvey and others, 1996).

This paper describes laboratory experiments being conducted under geochemical conditions similar to those in the perennial reach of Pinal Creek. The experiments are designed to study metal adsorption and coprecipitation by Mn oxide and carbonate phases that are currently forming in the perennial reach of the stream. Downstream trends in concentrations of dissolved Mn, Ni, and Co from November 1992 are presented first to describe the type of initial experiments needed to model reactive transport under present conditions in the stream.

METHODS OF FIELD SAMPLE COLLECTION, ANALYSIS, AND RESULTS

Surface-water and ground-water samples were collected in November, 1992, under base-flow conditions along a 6-km reach of Pinal Creek from the head of perennial flow to just above Inspiration Dam (fig. 1).
Figure 1. Locations of surface-water sites sampled November 1992.

The methods of sample collection are described in Harvey and Fuller (1996). Water samples for metal analysis were filtered in series through 0.45 and 0.001 μm (micron) pore-size filters, acidified, and analyzed by inductively coupled plasma emission spectrometry (ICP-AES).

Over this study reach, stream-water pH increased from 5.6 at the head of flow to 7.9 above Inspiration Dam (fig. 2). The downstream increase in pH results from carbon dioxide outgassing (Eychaner, 1991a). Over the first 0.5 km downstream from the head of flow, the concentration of dissolved Mn increased from 1.2 to 1.8 mM (millimolar) and was attributed to increased concentration of Mn in ground-water inflows (Harvey and others, 1996). The concentration of dissolved Mn decreased over the next 5 km by about 45 percent to 1 mM (fig. 2). Although the relative decrease was less than observed by Eychaner (1991b) in March 1990, it probably also is due largely to the formation of Mn oxide and carbonate. The Mn concentration in the colloidal size fraction at all sampling sites was less than the uncertainty in the difference between the 0.45- and 0.001-μm filtrates. The low Mn-colloid concentration suggests that the oxidation of dissolved Mn\(^{2+}\) occurs as a surface reaction on streambed sediments (Harvey and Fuller, 1996).

A similar downstream trend to manganese was observed for Ni (fig. 2). After an increase over the first 0.5 km of flow, Ni concentration decreased from 18 μM (micromolar) to 10 μM at 5.8 km; most of the decrease occurred within the first 3 km of flow. The colloidal Ni concentration also was not significant. The molar ratio of dissolved Ni to dissolved Mn (Ni/Mn ratio) decreased about 50 percent indicating a preferential loss of Ni relative to Mn within the first 1.5 km of flow (fig. 2) assuming a common source of dissolved Ni and Mn. Little subsequent change in Ni/Mn ratio is observed farther downstream. The preferential loss of Ni over Mn occurred within the reach where the rate of pH increase was greatest. The decrease in Ni concentration relative to Mn concentration may be due to sorption of Ni onto existing oxide phases in the
Figure 2. Dissolved constituents in Pinal Creek, November 1992. (Distances are in kilometers from the head of perennial flow located 6.2 kilometers upstream from Inspiration Dam in November 1992. Dissolved manganese is units of millimolar; nickel and cobalt in micromolar. Ratios of dissolved constituents are calculated in units of molar concentration.)
streambed and to Ni/Mn coprecipitation during Mn oxidation and precipitation (Hem and others, 1989). The relatively constant Ni/Mn ratio farther down­stream suggests that the subsequent decrease in Ni concentration occurs in conjunction with the decrease in Mn concentration. Although the observed down­stream decrease in metal concentration could, in part, be due to dilution, the modeling results of Eychaner (1991b) suggest that the changes in metal concentration were largely due to reaction processes.

The Co concentration increased from 1 to 5 μM within a 0.5-km reach from the head of flow (fig. 2) and subsequently decreased over the next 1 km by about a factor of two. Below this point, significant changes in Co concentration are not detectable because of greater uncertainty of low Co concentrations that are near the detection limit of ICP-AES. The Co to Mn molar ratio (Co/Mn ratio) decreased downstream to 1.5 km indicating a preferential loss of Co relative to Mn. Although the extraction of streambed materials suggest Ni and Co are primarily associated with Mn-oxide phases (Lind and Anderson, 1992), the partitioning processes controlling concentrations of dissolved Ni and Co have not been well characterized. A series of laboratory experiments is proposed to evaluate sorption processes that may control Ni and Co concentrations in Final Creek.

LABORATORY SORPTION EXPERIMENTS

Trace-metal concentrations in natural waters are typically less than saturation with respect to pure oxide and hydroxide phases and are commonly thought to be controlled by adsorption to mineral surfaces (Davis and Kent, 1990). The adsorption of metals onto Mn oxides increases with increasing pH. The relative binding strength to Mn oxides decreases in the following order: lead>Cu>Co>zinc>Ni (McKenzie, 1980). Metal adsorption onto synthetic θ-MnO₃ has been modeled by a surface complexation approach (Catts and Langmuir, 1986). In addition to adsorption onto Mn oxide surfaces, coprecipitation of trace metals (for example Ni, Cu and Co) can occur when dissolved metals are present during the oxidation and precipitation of the oxide phase; coprecipitation can result in the incorporation of trace metals into the Mn oxide structure (Hem and others, 1989). Uptake during coprecipitation can greatly exceed adsorption onto existing surfaces (Fuller and others, 1993), and may reduce the potential for desorption.

Because Mn forms a variety of oxide and carbonate phase in Pinal Creek (Lind and Hem, 1993), field-derived solid phases will be used to study metal sorption instead of synthetic Mn-oxide phases. Trace-metal coprecipitation with Mn during oxidation and precipitation will be studied using surface and ground water collected at the field site. These experiments will be similar to precipitation experiments used to determine the mineralogy of Mn precipitates (Hem and Lind, this volume). The pH will be increased to facilitate Mn oxidation by controlled reaeration to lower the partial pressure of carbon dioxide. Dissolved metal concentrations will be monitored as a function of time and pH to determine the amount of Ni and Co coprecipitated with the Mn phases.

The adsorption of trace metals by grain-size and mineralogic fractions of streambed sediments will be studied in batch as a function of metal concentration and pH using an artificial stream water (ASW). In contrast to the coprecipitation experiments, Mn will not precipitate from the ASW in these systems. The relative importance of trace-metal partitioning by adsorption and coprecipitation can then be compared.

The reversibility of metal sorption and the extent of desorption caused by changes in stream-water chemistry will be investigated. These experiments will include shifting the sorption equilibrium to favor desorption by decreasing either pH or dissolved metal concentration. Isotopic exchange will also be used to determine the fraction of adsorbed metals that can desorb (Davis and others, 1987). These experiments will be performed on streambed material containing ambient sorbed-metal concentrations as well as on Mn precipitates and sediments from the sorption experiments outlined above. The reversibility studies may help identify the important sorption processes for inclusion in solute-transport models for Pinal Creek.

SUMMARY

A series of laboratory trace-metal (Ni, Co, Cu) adsorption, coprecipitation, and reversibility experiments are being conducted using field-derived materials under geochemical conditions similar to those in the perennial flow of Pinal Creek. The experimental results will help identify the importance of various partitioning processes between solution and mineral phases and provide sorption-desorption coefficients for use in reactive transport modeling of trace metals in the stream. For example, under present conditions in Pinal
Creek, Ni may be removed during transport by adsorption onto existing phases in streambed sediments as well as by coprecipitation with Mn-oxide phases. The magnitude of uptake and desorption potential may differ significantly for these two sorption processes.

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Relations Among Algal Species and Chemical Gradients in Pinal Creek, near Globe, Arizona

By Patrice H. Spindler¹ and Milton R. Sommerfeld²

Abstract

The relations among algal species and water chemistry in Pinal Creek, near Globe, Arizona, were investigated. Periphyton, water, and sediment samples were collected from seven sites during 1991-92. Fourteen species of algae and 16 chemical properties were selected for correlation and cluster analyses. Three major algal associations in Pinal Creek were identified by cluster analysis: an acid- and metal-tolerant association at upstream sites, an alkalophilous association at downstream sites, and an association of ubiquitously distributed opportunistic species. Indicator species of the acid- and metal-rich environment at upstream sites were Microspora stagnorum, Surirella minuta and Ulothrix variabilis. The exclusion of Nitzschia linearis and Vaucheria geminata from upstream sites and their abundance at downstream sites suggest that these species are acid and metal intolerant.

INTRODUCTION

Algal communities are valuable in water-quality assessment because they are very responsive to physicochemical changes in habitat (Stevenson and Lowe, 1986). The taxonomic composition of the algal community provides an alternative to traditional chemical methods for assessing the effect of acid mine drainage on a stream ecosystem. Specific taxa and species richness and diversity indices have been used to characterize streams affected by acidic mine drainage. English streams contaminated by metals are characterized by a Microspora community whereas streams with low concentrations of metals contain a Zynematales community of Spirogyra and Mougeotia species (Foster, 1982). Increasing concentrations of zinc shifted the algal community from diatoms to green or blue-green algae in an outdoor stream mesocosm in Virginia (Genter and others, 1987). Low species richness (Stokes, 1983) and diversity (Hargreaves and others, 1975) have also been used as indicators of impaired water quality.

Pinal Creek receives drainage from an upstream copper mining district near Globe-Miami, Arizona. Significant increases in pH and significant decreases in metal concentrations, such as manganese and nickel occur with distance downstream (Spindler, 1993). The purpose of this paper is to characterize the algal community and its relation to the water quality of Pinal Creek. This research was partly funded by a grant from the U.S. Geological Survey (order # 230102).

METHODS

Samples of algae, water and sediment were collected at seven sampling sites within a 6-km reach of Pinal Creek during May, July, and October 1991 and January 1992. The sampling sites were located at distances of 0.0, 1.0, 1.5, 2.0, 2.5, 4.5, and 5.5 kilometers from the headwater (fig. 1). These sites are hereafter referred to by sites 1-7, respectively.

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Figure 1. Area of study.
Site 2 was located at Setka Ranch (station 09498380) and site 7 was located at Inspiration Dam (station 09498400).

Three replicate algae samples were collected at each site. Each sample consisted of a composite of six individual samples collected along a randomly determined transect. A 5-cm plastic cylinder emplaced to a depth of 2 cm in the sediment was used as a benthic sampler to collect consistent-volume, 39 cm³ periphyton-containing sediment samples. Algal material was separated from sediments by the sedimentation method (American Public Health Association, 1985). Diatom and non-diatom species were prepared and counted separately, because non-diatoms degrade rapidly after sample collection whereas diatoms can be permanently mounted. Non-diatom species abundances were enumerated from unpreserved samples by use of a Sedgewick-Rafter chamber and an inverted microscope equipped with an ocular grid. Diatom species were enumerated from permanent burn mounts of sample material (Stevenson and Lowe, 1986) by use of a light-transmission microscope equipped with an ocular micrometer. Taxonomic identifications were made for 1,000 cells in each sample—500 diatoms and 500 non-diatoms.

Four abundance categories (dominant, common, infrequent, rare) were used to characterize the frequency of occurrence of each species for each sample event. Only the dominant species were selected for cluster analysis and correlation analysis to identify the major associations of algae and their relations to water chemistry.

Algal associations were identified in a dendogram obtained by cluster analysis using SYSTAT software (Wilkinson, 1988). Cluster analysis was based on Ward's minimum variance method, which joins successive groups using their squared Euclidean distances. Correlations between each of 14 algal species and 16 chemical properties were analyzed by use of the Number Cruncher Statistical System (Hintze, 1985).

Three replicate, filtered water samples and four replicate, composited sediment samples were collected from each site. Water samples were analyzed for alkalinity, ortho-phosphate, and nitrate following standard analytical methods (U.S. Environmental Protection Agency, 1983). Water and sediment samples were analyzed for the metals cobalt, copper, iron, manganese, nickel and zinc following procedures outlined in Standard Methods (American Public Health Association, 1985). Only ranges of values for each property have been presented in this paper. Additional detail about chemical methods and results can be found in Spindler (1993).

RESULTS

Three major algal species associations in Pinal Creek were identified by cluster analysis (fig. 2). The first algal association consisted of *Caloneis hultenii*, *Microspora quadrata*, *M. stagnorum*, *Nitzschia ignorata*, *Surirella minuta*, *Tribonema bombycinum*, *Ulothrix subtilissima*, and *U. variabilis*. The second algal association consisted of *Cyclotella meneghiniana*, *Nitzschia linearis*, and *Vaucheria geminata*. The third algal association consisted of *Nitzschia palea*, *Surirella angustata*, and *Tribonema minus*.

The first algal association displayed positive correlations with metals and sulfate concentrations and negative correlations with pH and alkalinity (table 1). Several of the species in this association have been reported in the literature as tolerant of acidic mine drainage. Foster (1982) indicated that a grouping of *Microspora* species could be termed an indicator community for heavy-metal contamination. Whitton (1970) concluded that *Microspora* and *Ulothrix* species are resistant to copper, lead, and zinc. *Ulothrix subtilissima* was found upstream and far downstream of acidic mine drainage, whereas *Ulothrix variabilis* was ubiquitous in an Arizona stream receiving acidic mine drainage (Lampkin and Sommerfeld, 1982). Palmer (1977) placed *Surirella ovata*, synonymous with *S. minuta*, on a list of the 80 most tolerant species, although the genus had not been previously listed as an indicator species for acidic mine drainage. *Surirella minuta* tolerates a wide range in pH in Pinal Creek. This first algal association was found in the greatest abundance at upstream sites in Pinal Creek, where pH was less than 7.0 units and metal concentrations were highest (Spindler, 1993).

The second algal association composed of *Cyclotella meneghiniana*, *Nitzschia linearis*, and *Vaucheria geminata* species displayed positive correlations with pH and alkalinity and negative correlations with concentrations of metals and sulfate.
Figure 2. Dendrogram of algal associations in Pinal Creek. Mean abundances for dominant species distributed among seven sites were compared using Ward's minimum variance method. Species were grouped using their squared Euclidean distances.
Table 1. Coefficients of correlation (r) between algal species abundances and selected chemical constituents and pH, Pinal Creek, Arizona

[Species abundances were natural log transformed means from four seasonal sampling events for each of seven sites. Chemical properties were means of four seasonal sampling events for each of seven sites; only r values significant at p < 0.05 were listed, except where noted; Alk, alkalinity]

<table>
<thead>
<tr>
<th>Species</th>
<th>Concentration ranges (mg/L) and correlation coefficients (r)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Alk 45-99</td>
</tr>
<tr>
<td>Association 1</td>
<td></td>
</tr>
<tr>
<td>Caloneis hultenii Peters. var. hultenii</td>
<td>-.71</td>
</tr>
<tr>
<td>Microspora quadrata Hazen</td>
<td></td>
</tr>
<tr>
<td>Microspora stagnorum (Kuetz.) Lagerheim</td>
<td>-.89</td>
</tr>
<tr>
<td>Nitzschia ignorata Krasske</td>
<td></td>
</tr>
<tr>
<td>Surirella minuta Breb.</td>
<td>-.92</td>
</tr>
<tr>
<td>Tribonema bombycinum (C.A.Ag)Derbes,Solier</td>
<td>-.81</td>
</tr>
<tr>
<td>Ulothrix subtilissima Rabenhorst</td>
<td>-.78</td>
</tr>
<tr>
<td>Ulothrix variabilis Kuetz.</td>
<td>-.97</td>
</tr>
</tbody>
</table>

| Association 2                               |             |            |              |              |              |              |          |              |             |
| Cyclotella meneghiniana Kuetz.               | .77         |            |              | -.77         |              |              |          |              |             |
| Nitzschia linearis W. Smith                 | .98         | .88        | -.85         | -.88         | -.78         | -.76         | .77      |              | -.76         |
| Vaucheria geminata (Vauch.) De Candolle     | .89         | .89        | -.77         | .89          | .89          | .89          | -.77    |              | .89          |

| Association 3                               |             |            |              |              |              |              |          |              |             |
| Nitzschia palea (Kuetz.) W. Smith           |             |            |              |              |              |              |          | .69          |              |
| Surirella angustata Kuetz.                   |             |            |              |              |              |              |          |              |             |
| Tribonema minus (Wille) Hazen                | -.77        |            |              |              |              |              |          |              | -.77         |

1Significant at p < 0.100
Nitzschia linearis and Vaucheria geminata were listed by Palmer (1977) as clean-water species. Vaucheria geminata had the most limited distribution of all the dominant species; it was found only at downstream sites 4-7. Lampkin and Sommerfeld (1982) found that Vaucheria was not present in the reach of Lynx Creek that receives acidic mine drainage but was present in a tributary to Lynx Creek. These data and observations suggest that V geminata may be an indicator of the recovery zone in Final Creek, where pH increases to the range of 7.0 to 8.0 and alkalinity concentration increases to greater than 90 mg/L. Rushforth, and others (1981) showed that Cyclotella meneghiniana showed a preference for high concentrations of manganese and selenium and was also positively correlated with high concentrations of aluminum, copper, iron, and lead. Under these conditions, one might expect to find C. meneghiniana near the beginning of perennial flow, where concentrations of these metals were highest. The fact that C. meneghiniana was found in part of Pinal Creek where acidic mine drainage was minimal suggests that other factors may play a role in determining its niche. This association was most abundant at downstream sites in Pinal Creek, where pH was higher and metal concentrations were lower relative to upstream sites.

The third algal group, which consists of the species Nitzschia palea, Surirella angustata, and Tribonema minus, was distributed throughout the study reach and was characterized by a lack of strong correlations with high or low pH or metal concentrations. Nitzschia palea has been characterized as tolerant of low pH (Hargreaves and others, 1975), as an indicator of elevated copper and chromium concentrations (Palmer, 1959), and as an indicator of elevated aluminum, arsenic, iron, manganese, and selenium concentrations (Rushforth and others, 1981). Surirella and Tribonema are among the 60 most pollution tolerant genera listed by Palmer (1977). This group of algae did not form a specific association, defined by increased density under a particular set of chemical conditions. Rather, these species shared the common attribute of being tolerant of a wide range of pH and metal concentrations and of being ubiquitously distributed in Pinal Creek. Foster (1982) concluded that the most abundant algae at sites where metal concentrations were high also were found at sites where metals were present in a broad range of concentrations. Such species have adapted to chemically disturbed environments but are not strictly indicative of a particular metal. According to results of the present study, these three species have apparently adapted to a chemically disturbed environment having a pH range of about 2 units and a range in concentrations of metals.

The shift in chemical characteristics within a 6-km perennial reach of Pinal Creek is reflected by a corresponding shift in the algal composition. If the water that continues to move downstream in Pinal Creek continues to be acidic (Eychaner, 1989), a corresponding shift in the algal associations could be expected, such as the dislocation of readily visible Vaucheria mats from sites 4-7. The disappearance of this genus may provide an early indication of changing stream conditions associated with increasing acidity and metal concentrations.

SUMMARY

The algae of Pinal Creek are distributed in a pattern that reflects the response of the algae to changing chemical conditions. Three major algal associations in Pinal Creek were identified in this study: (1) an acid- and metal-tolerant association at upstream sites, (2) an alkalophilous association at downstream sites, and (3) an association of ubiquitously distributed opportunistic species. Indicator species of the acid- and metal-rich environment at upstream sites were Microspora stagnorum, Surirella minuta, and Ulothrix variabilis. The absence of Nitzschia linearis and Vaucheria geminata from upstream sites and their abundance at downstream sites suggests that these species are acid and metal intolerant. A follow-up study in five to 10 years is recommended to determine whether algae distribution will continue to change in relation to stream conditions.

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