U.S. Geological Survey Toxic Substances Hydrology Program--Proceedings of the technical meeting, Monterey, California, March 11-15, 1991

By Gail E. Mallard and David A. Aronson, editors

U.S. GEOLOGICAL SURVEY

Water-Resources Investigations Report 91-4034

U.S. DEPARTMENT OF THE INTERIOR
March 3, 1849

Reston, Virginia
1991

U.S. DEPARTMENT OF THE INTERIOR

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PREFACE

The U.S. Geological Survey's Toxic Substances Hydrology Program provides earth-science information needed to understand the movement and fate of hazardous substances in the Nation's ground and surface waters. To do this, the program: (1) conducts laboratory and field research on the physical, chemical, and biological processes controlling contaminant transport and transformation; (2) develops new analytical methods and sampling techniques; and (3) investigates the relationships among various human activities, environmental characteristics, and regional patterns of water quality.

Much new information has become available as the result of studies conducted by the Toxic Substances Hydrology Program. In order to facilitate exchange of information among the many scientists working on relevant research, a series of technical meetings have been held in Tucson, Arizona (1984), Cape Cod, Massachusetts (1985), Denver, Colorado (1987), Pensacola, Florida (1987), and Phoenix, Arizona (1988). These meetings provide an opportunity to present research results and to plan new field efforts. This report documents the results of research presented at a technical meeting held in Monterey, California, in March 1991.

The report is organized into 13 chapters that focus on field-site investigations, nonpoint source research, or methods research. Chapters A, B, D, F, G, and I through M present results of research, still in progress, on the occurrence and movement of hazardous substances within specific hydrologic systems. These intensive interdisciplinary investigations represent a key element of the research approach taken by the Toxic Substances Hydrology Program. The sites, selected to study a variety of contaminants, provide a focus for both process-oriented and methods-development research. Each chapter presents the results of research on specific types of contaminants in specific environments. Ground-water quality problems currently under investigation include contamination by crude oil, gasoline, sewage, trace metals, pesticides and chlorinated organic solvents. The river systems being studied have been affected by industrial effluent, mine drainage, agricultural chemicals, and urban and suburban development. The first paper in each of these chapters provides an overview of the hydrologic setting and describes the nature and history of the contamination problem. Subsequent papers report the results of a specific research problem.

Chapters C and E describe results of research on nonpoint sources of ground- and surface-water contamination. The ultimate goal of these studies is to develop study procedures that can be used to understand how land use practices affect water quality. Agriculture is one of the most significant nonpoint sources of contamination and many of the papers in these chapters deal with agricultural chemicals and the effect of agricultural practices on water resources.

Chapter H describes research methods and techniques used to study toxic substances. Papers in this chapter include analytical methodology, chemical modeling techniques, and both field and laboratory methods from the disciplines of chemistry, geology, and physical hydrology. This diversity of topics is a good measure of the range of techniques and approaches required for understanding the transport and fate of hazardous substances in ground and surface waters.

The information in this report should help to expand the scientific basis for management decisions to prevent or mitigate contamination of the Nation's waters. The papers describing results of work at the field sites demonstrate the degree of understanding that can be gained from intensive, interdisciplinary research. This understanding should be transferable to studies of similar types of contaminants. Research on nonpoint sources of contamination has helped to better define the effects of agriculture and other human activities on water quality. The analytical and interpretive methods reported in this volume will be useful to scientists involved in studies of natural water quality as well as to those studying contaminated waters.

Gail E. Mallard, Coordinator
Toxic Substances Hydrology Program

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By Stephen P. Garabedian[1] *and* Denis R. LeBlanc[1]

ABSTRACT

The Cape Cod Toxic-Substances Hydrology Research site, located in Falmouth, Massachusetts, is the focus for a number of field research projects studying subsurface contaminant hydrology, inorganic and organic geochemistry, and microbiology. Past research efforts at the site have involved the definition and description of the extent of aquifer contamination in a sewage plume originating from the Otis Air Base sewage-treatment facility. Current research at the site is reviewed in a synopsis of 25 papers. These papers include efforts to characterize specific physical, chemical, and microbiological processes affecting the transport and fate of solutes and bacteria at the site. 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 meters, and large-scale investigations of the sewage plume with specialized sampling methods.

INTRODUCTION

The U.S. Geological Survey (USGS) Cape Cod Toxic-Substances Hydrology Research site is located in the northern part of Falmouth, Mass., on Cape Cod (fig. 1). This site is the focus of research on the geologic, hydrologic, chemical, and microbiological processes that affect 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 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 volume. Earlier summaries of research at the Cape Cod site can be found in reports by LeBlanc (1984b), Franks (1987), Ragone (1988), and Mallard and Ragone (1989).

SITE DESCRIPTION

The study area is on a broad sand and gravel 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, which typically are 150 to 270 m (meters) wide and 10 m deep, do not contain streams but have wetlands at their southern ends.

A hydrogeologic section showing the vertical distribution of sediment types is shown in figure 2. The top 30 to 50 m of sediment are a glacial outwash composed of stratified, medium to coarse sand with some gravel. In the northern part of the study area, the sand and gravel overlies fine sand and silt. To the south, the outwash overlies fine sand, silt, and sandy till. The till contains lenses of clay, silt, sand, and gravel. These unconsolidated sediments overlie a crystalline (granodiorite) bedrock surface, which generally slopes from west to east through the study area.

On the basis of measured values for similar sediments on Cape Cod, LeBlanc (1984c) estimated that the horizontal hydraulic conductivity of 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 indicated that the horizontal hydraulic conductivity of the sand and gravel may be locally as high as 120 m/d (Garabedian and others, 1988). The horizontal hydraulic conductivity of the underlying fine sand and sandy till 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 surface 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 aquifer recharge 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, about 45 percent of the total precipitation (LeBlanc, 1984c). 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

LeBlanc (1984b,c) described the extent of contamination in the aquifer caused by the disposal of treated sewage onto infiltration beds at Otis Air Base (fig. 1). In 1979, the plume of contaminated ground water, formed by disposal since 1936, was 0.8 to 1.1 km (kilometers) wide, 23 m thick, and more than 3.4 km long (figs. 1,2). 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.

The plume of sewage-contaminated ground water is characterized by elevated concentrations of dissolved solids, boron, chloride, sodium, phosphorus, ammonium, nitrate,

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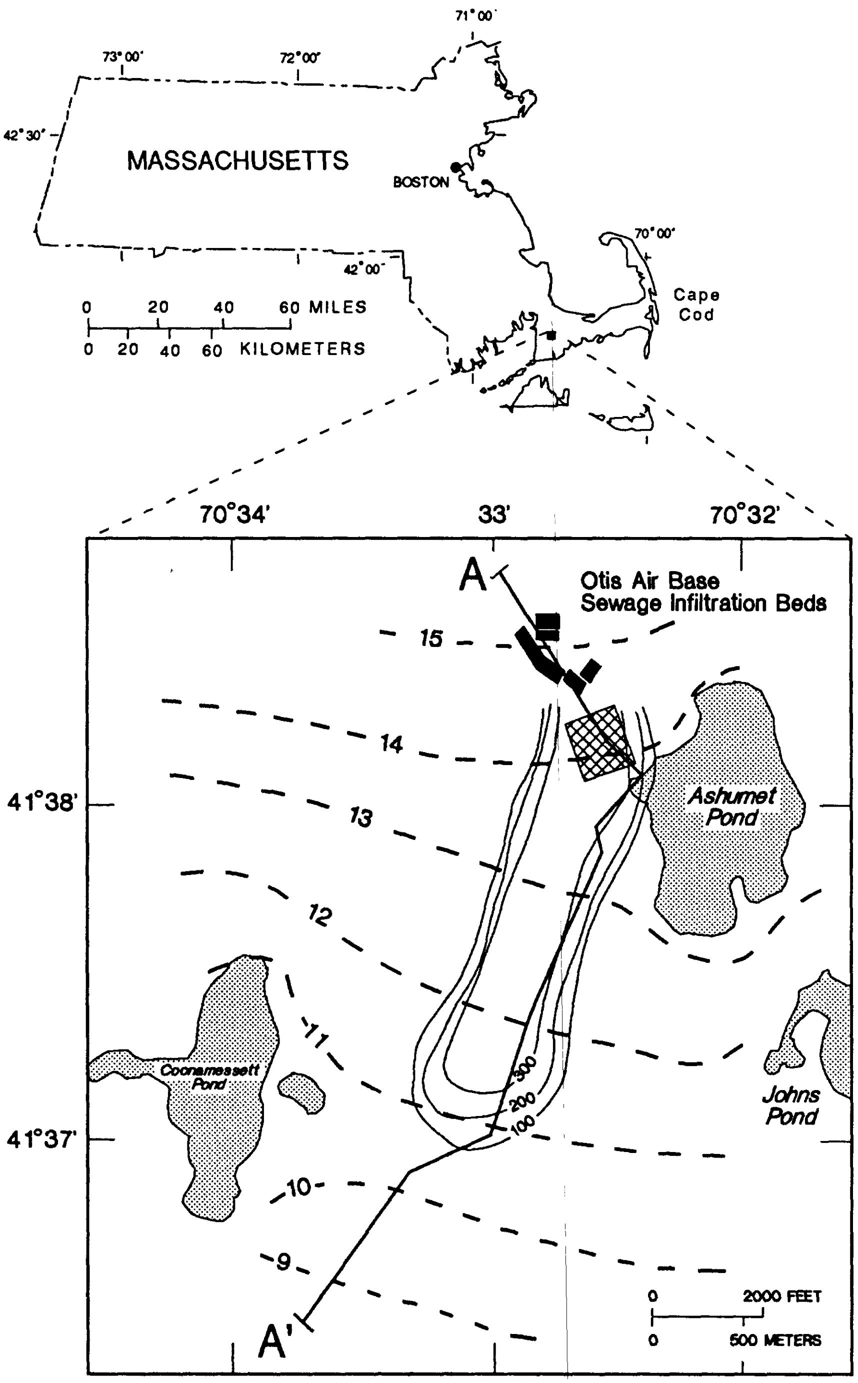
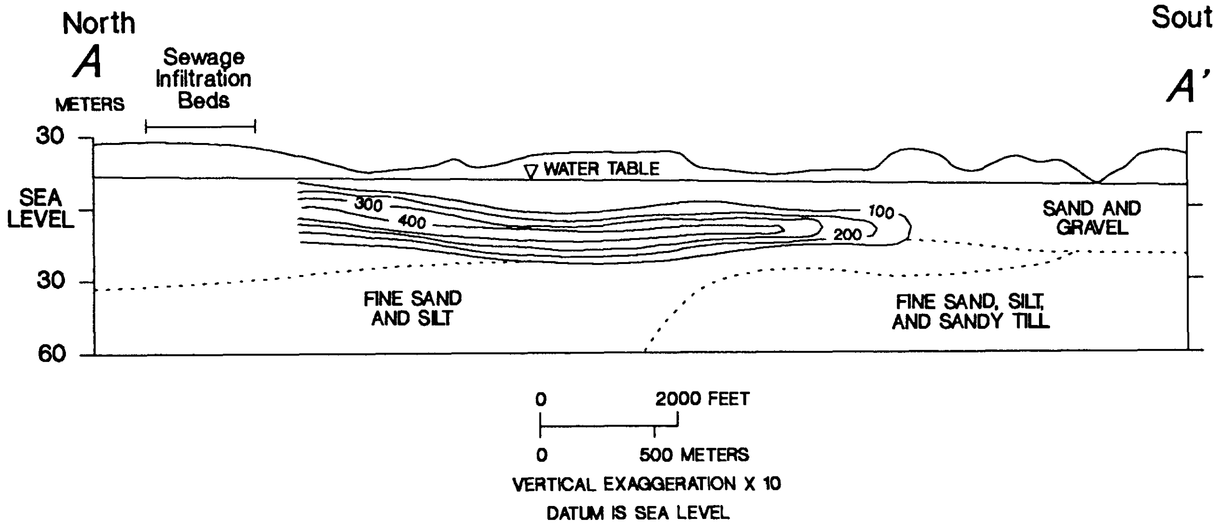
[1] U.S. Geological Survey, Marlborough, Mass.


71°00'
73°00'
72°00'
42°30'
MASSACHUSETTS
BOSTON
70°00'
42°00'
Cape Cod
0 20 40 60 MILES
0 20 40 60 KILOMETERS
70°34'
33'
70°32'
A
Otis Air Base Sewage Infiltration Beds
15
14
13
12
11
10
9
41°38'
41°37'
Ashumet Pond
Coonamessett Pond
Johns Pond
300
200
100
A'
0 2000 FEET
0 500 METERS

EXPLANATION

▨	TRACER-TEST SITE -- Shows area in figure 3.
—— 100 ——	LINE OF EQUAL BORON CONCENTRATION, 1978-79-- Concentrations in micrograms per liter.
- - 10 - -	WATER-TABLE CONTOUR, NOVEMBER 1979-- Altitude of water table in meters. Datum is sea level.
A⊢—⊣A'	LINE OF SECTION SHOWN IN FIGURE 2.

Figure 1. Location of study area, showing sewage plume and tracer-test site. (Modified from LeBlanc, 1984c, fig. 16.)



EXPLANATION

—400— LINE OF EQUAL BORON CONCENTRATION, 1978-79 -- Concentrations in micrograms per liter.

Figure 2. Vertical location of sewage plume and geohydrologic units. Line of section shown in figure 1. (Modified from LeBlanc, 1984c, figs. 9 and 17.)

detergents (LeBlanc, 1984c) and, in some locations, volatile organic compounds (VOC) (Thurman and others, 1984; Barber and others, 1988). Boron, chloride, and sodium appear to be conservative and nonreactive, and are attenuated primarily by hydrodynamic dispersion. Phosphorus movement is greatly retarded by colloidal precipitation (Gschwend and Reynolds, 1987; Backhus and Gschwend, 1990) and adsorption onto the sediments. Although a maximum nitrate concentration of 16 mg/L (milligrams per liter)(as nitrogen (N)) has been detected in the sewage effluent, the concentration in the center of the plume immediately downgradient of the disposal beds is below detection (LeBlanc, 1984c; Ceazan and others, 1989) owing to microbially-mediated denitrification (Smith, Howes, and Duff, 1991a). Within 1.5 km of the disposal beds, the predominant nitrogen species in the plume is ammonium. Beyond 1.8 km from the beds, the predominant nitrogen species changes to nitrate, with concentrations of about 3 to 4 mg/L. This distribution of ammonium is caused, in part, by adsorption onto the aquifer sediments (Ceazan and others, 1989), which retards the movement of ammonium. Detergent concentrations exceed 0.5 mg/L methylene-blue-active substances (MBAS) 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).

Elevated VOC concentrations are present in two zones in the study area, one which is immediately downgradient from the disposal beds and the other 500 to 2,600 m downgradient from the beds. 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 that is farther 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). VOC concentrations in the downgradient zone exceed 50 µg/L (micrograms per liter), which suggests that the VOC's are mobile and not readily degraded in the sandy aquifer (Barber, 1988; Barber and others, 1988).

Bacterial population counts as large as 2x 10^6/mL (per milliliter) are found in ground water near the disposal beds; these counts decrease to about 2.5x 10^5/mL farther 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 decrease from 12 mg/L to less than 2 mg/L over the same distance (Thurman and others, 1986). The decrease in bacterial numbers with distance, particularly bacteria smaller than 0.4 micrometers in diameter, also suggests that transport and filtering of bacteria is occurring (Harvey and others, 1989). Assays of microbial activity have been made for both ground water and aquifer sediments because more than 90 percent of 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 samples collected from a 1- to 2-m-thick zone near the top of the plume, demonstrating the need for close-interval vertical sampling (Smith, Harvey, and LeBlanc, 1991).

CURRENT RESEARCH

Current research at the Cape Cod site has focused on the development and use of laboratory experiments, *in-situ* tests, and specialized sampling methods to improve understanding of transport processes for contaminants in the sewage plume and solutes not found in the plume.

Physical Transport

A major research objective at the Cape Cod site has been to relate the dispersion of solutes to the heterogeneity of aquifer 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 conducted from 1985-87 (Garabedian and others, 1991; LeBlanc, Garabedian, Hess, Gelhar, Quadri, Stollenwerk, and Wood, 1991). Bromide, a nonreactive tracer, was monitored with a three-dimensional array of 9,840 sampling points in a sand and gravel pit as it moved 280 m through the aquifer (fig. 3). The spatial-moments analysis indicates that the aquifer dispersivity is about 1.0 m in the direction of flow, 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 analytical and numerical models of density-dependent flow (LeBlanc and Celia, 1991, this Proceedings) to the large-scale natural-gradient tracer test shows that the density contrast 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 early part of the test. The analytical models also show that the amount of density-dependent sinking is influenced by the anisotropy of hydraulic conductivity. Simulations using a numerical model indicate that downward movement is enhanced by small dispersion and a large source size.

Hess and others (1991, this Proceedings) present estimates of aquifer macrodispersivity using the statistical properties of the hydraulic-conductivity distribution in the theoretical stochastic transport equations of Gelhar and Axness (1983). The statistics were obtained from the analysis of nearly 1,500 measurements of hydraulic conductivity at the Cape Cod site 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 asymptotic longitudinal macrodispersivity is 0.35 to 0.78 m; this range is similar to the longitudinal dispersivity observed in the large-scale tracer test.

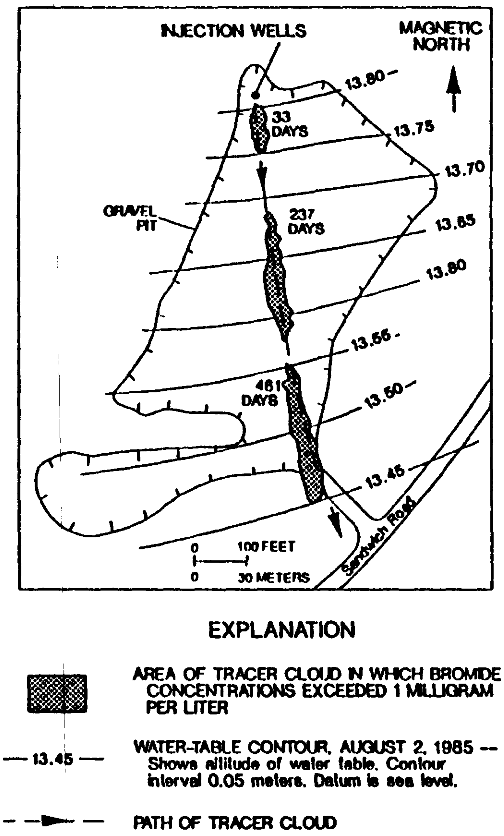

INJECTION WELLS
MAGNETIC NORTH
13.80
13.75
13.70
13.65
13.60
13.55
13.50
13.45
33 DAYS
237 DAYS
461 DAYS
GRAVEL PIT
Sandwich Road
0 100 FEET
0 30 METERS
EXPLANATION
AREA OF TRACER CLOUD IN WHICH BROMIDE CONCENTRATIONS EXCEEDED 1 MILLIGRAM PER LITER
— 13.45 — WATER-TABLE CONTOUR, AUGUST 2, 1985 -- Shows altitude of water table. Contour interval 0.05 meters. Datum is sea level.
PATH OF TRACER CLOUD

Figure 3. Tracer-test site in abandoned gravel pit, showing water table and path of bromide tracer cloud. Location of map shown in figure 1. (Modified from LeBlanc, Garabedian, Hess, Gelhar, Quadri, Stollenwerk, and Wood, 1991, fig. 4.)

Analysis of nuclear logs has been used at the Cape Cod site to estimate the amount of formation disturbance from drilling (Morin and others, 1988) and was also used to estimate hydraulic-conductivity variations near the location of the large-scale tracer test (Morin and Hess, 1991, this Proceedings). An algorithm based on the Kozeny-Carmen equation was developed for predicting hydraulic conductivity from nuclear logs using the logs and flowmeter results from three wells. This algorithm was applied to the nuclear logs from a fourth well. The resulting hydraulic conductivity profile indicates that the algorithm is unsatisfactory for defining quantitative profiles of hydraulic conductivity from nuclear logs and that the incorporation of additional data on the grain-size distribution may be necessary for accurate predictions. However, this method accurately reproduces average hydraulic-conductivity statistics (mean, variance, vertical correlation scale) and may provide statistical parameters needed for the prediction of macrodispersivity in aquifers.

Three-dimensional ground-penetrating radar (GPR) surveys were conducted at the site of the large-scale tracer test to delineate near-surface geologic conditions (Knoll and others, 1991, this Proceedings). Processed sections from the three-dimensional data demonstrate the ability of GPR to map the water table and apparent depositional features in the sand and gravel aquifer to a depth of 12 m. Preliminary experiments yielded average electromagnetic-propagation velocities for the saturated and unsaturated zones of 0.2 m/ns (meters per nanosecond) and 0.45 m/ns, respectively.

In addition to the above efforts to characterize the aquifer properties near the location of the large-scale tracer test, a slug-testing program was carried out at the Cape Cod site to provide a large-scale characterization of aquifer hydraulic conductivity across the whole study area (Springer and Gelhar, 1991, this Proceedings). A total of 338 observation wells were tested in a 44 square-kilometer area. Preliminary analysis shows a large range in hydraulic conductivity, from 0.08 to 480 m/d, with a geometric mean of 43 m/d. The standard deviation of the natural log of the hydraulic-conductivity distribution is 1.4. Large-scale trends across the study area are evident from the results, particularly a lower value of hydraulic conductivity in the finer sediments beneath the sand and gravel (fig. 2).

The effects of variations in physical properties on unsaturated flow and solute transport in heterogeneous aquifers were observed in detail during an infiltration experiment conducted in the unsaturated zone of the sand and gravel aquifer (LeBlanc, Rudolph, Kachanoski, and Celia, 1991, this Proceedings). Soil-water content, pressure, and solute concentration were measured on a test plot that was 2 m wide and 10 m long using 168 pairs of time-domain reflectrometry probes and 112 suction-lysimeter/tensiometers installed to a depth of 2 m. The plot was irrigated under both steady-flow and transient-flow conditions using sprinkler nozzles set about 1.5 m above ground surface. Analysis of the data will focus on the spatial variability of the response of the unsaturated zone to irrigation and the ability of numerical models to simulate the experimental results.

Inorganic Geochemistry

In addition to measuring dispersion in the aquifer, the large-scale natural-gradient tracer test was also conducted to determine geochemical controls on reactive transport in a heterogeneous aquifer. Two reactive tracers, lithium and molybdate, were monitored as part of the tracer test and were found to be significantly retarded relative to bromide (LeBlanc, Garabedian, Hess, Gelhar, Quadri, Stollenwerk, and Wood, 1991). For lithium, a cation, adsorption occurs on the mineral surfaces and, more significantly, inside the weathered feldspar grains (Wood and others, 1990), where adsorption is controlled by diffusion into micropores. The diffusion-controlled adsorption resulted in a skewed distribution of lithium, with highest 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 phosphate, an oxyanion that competes with molybdate for adsorption sites (Stollenwerk and Grove, 1987; Stollenwerk and Kipp, 1990). Laboratory experiments were used to determine the effects of changes in chemical composition of ground water and ferrihydrite content of the aquifer sediment on the sorption of molybdate (Stollenwerk, 1991, this Proceedings). It was found that molybdate sorption decreases with increasing hydrogen-ion, sulfate, and phosphate concentrations, and increases with increasing ferrihydrite content. A diffuse-layer surface-complexation model, coupled with an aqueous geochemical speciation program (MINTEQA2), was used to simulate the sorption of molybdate onto the aquifer sediment. A single set of equilibrium constants could be used to simulate the experimental results over the entire range of geochemical conditions.

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 (Kent and others, 1989; Davis, Kent, Rea, Garabedian, and Anderson (1991, this Proceedings). The results of tracer tests with Zn (zinc), Cr (chromium), and Se (selenium) showed, in some cases, significant changes in speciation during transport. The reactions and processes that affected the observed test results include adsorption-desorption, aqueous complexation, and oxidation-reduction reactions.

The results of laboratory studies of Cr reduction and sorption on aquifer sediments are presented in Anderson and others (1991, this Proceedings) and Davis, Waite, Kent, and Anderson (1991, this Proceedings). Experiments with freshly collected sediments from the oxygen-rich zone above the sewage plume in the gravel pit showed evidence of Cr(VI) reduction as well as adsorption. Cr(VI) adsorption was greatest under the low pH and low ionic strength conditions that characterize this uncontaminated zone above the sewage plume (Anderson and others, 1991, this Proceedings). The results of experiments with suboxic materials collected from the sewage-contaminated zone (suboxic water) showed that, although adsorption of Cr(VI) is low under these conditions, significant quantities Cr(VI) are reduced to Cr(III) (Davis, Waite, Kent, and Anderson, 1991, this Proceedings). Reduction of Cr(VI) in both the oxic and suboxic experiments led to irreversible sorption of Cr(III). These results are consistent with observations of loss of Cr(VI) (without retardation) in small-scale tracer tests conducted in the sewage-contaminated zone in the gravel pit (Davis, Kent, Rea, Garabedian, and Anderson, 1991, this Proceedings).

Small-scale tracer tests revealed differences in the transport of Zn in the presence of EDTA (ethylenediaminetetracetic acid) in the uncontaminated recharge water and the underlying sewage-contaminated water owing to differences in the chemistry of the two zones (Kent and others, 1991, this Proceedings). Tracer tests in the recharge zone showed significant retardation of Zn relative to the conservative tracer Br (bromide). EDTA was also retarded in the recharge zone, but to a lesser extent than was Zn. Dissolution of Fe (iron) from constituents of the aquifer material in the low-pH recharge zone resulted in displacement of Zn from EDTA complexes and then extensive Zn adsorption onto the aquifer material. Transport of EDTA and Zn in the sewage-contaminated zone was conservative. Because the solubility of hydrous Fe oxides is low at the near-neutral pH values characteristic of the sewage-contaminated zone, displacement of Zn from its complexes with EDTA and subsequent adsorption of Zn did not occur in this zone.

The objectives and approach of a study to identify the geochemical parameters controlling metal-ion sorption and to describe their spatial variability in the sand and gravel aquifer are outlined by Fuller and others (1991, this Proceedings). The goal of this research is to examine the influence of spatial variability in these parameters on the transport of surface-reactive solutes in ground-water systems. The results will be used in conjunction with tracer-test studies of metal transport (Davis, Kent, Rea, Garabedian, and Anderson, 1991, this Proceedings; Davis, Kent, Rea, Maest, and Garabedian, 1991) to develop coupled solute-transport and reaction models that incorporate the observed spatial variability in (1) geochemical parameters used to estimate sorbent abundance, (2) metal sorption coefficients, and (3) hydraulic conductivity.

As a complement to the smaller-scale tracer test studies, sampling of the sewage plume has shown that discharge of sewage effluent into the sand and gravel aquifer has resulted in contamination of the aquifer with Zn (Rea and others, 1991, this Proceedings). Mobility of Zn in the ground water is retarded by adsorption onto the aquifer material. The extent of Zn adsorption is a function of pH, and at the pH of the recharge water (5.0) Zn adsorption onto the aquifer material is extensive but not complete. Treated sewage is buffered at pH 6.0, and at this pH Zn is immobilized by adsorption onto the sand. The increase in pH with depth in going from the recharge zone to the sewage-contaminated zone of the aquifer gives rise to a region at the upper margin of the sewage-contaminated zone where the pH is low enough for Zn to be mobile, although greatly retarded by adsorption. Sampling to determine the spatial distribution of Zn downgradient from the infiltration beds shows that Zn has moved only about 350 m after more than 50 years of disposal, which is consistent with extensive retardation of Zn.

Thirty-six wells in the uncontaminated part of the aquifer were sampled to investigate larger-scale variations in aquifer geochemistry (Lee, 1991, this Proceedings). Analyses of these samples showed consistent increases in dissolved silica, pH, and dissolved solids with increasing depth, which are likely caused by incongruent dissolution of feldspar minerals to kaolinite. The degree of feldspar weathering is constrained by variations in the concentrations of dissolved CO_2 (carbon dioxide) in the recharge water infiltrating through the unsaturated zone. The magnitude of CO_2 concentrations in the unsaturated zone are likely related to land cover and land-use practices in the study area.

Organic Geochemistry

The mix of organic compounds in the sewage plume is very complex, and a hierarchical analytical approach was required to determine the predominant compounds present (Barber, Thurman, Field, Leenheer, and LeBlanc, 1991, this Proceedings). The major organic contaminants fall into two classes: volatile chlorinated hydrocarbons (VCH) and surfactant-derived products. The VCH do not appear to be undergoing biodegradation or significant sorption to the aquifer sediments. In contrast, the distributions of anionic and nonionic surfactants are controlled by biodegradation and sorption to the aquifer sediments.

A combined field and laboratory study was conducted that compared the results from purge and trap gas chromatography/mass spectrometry (PT-GC/MS) and purgeable organic chloride (POCL) analysis for measuring VCH (Barber, Thurman, Takahashi, and Noriega, 1991, this Proceedings). Distilled-water spike-and-recovery experiments indicated that, at concentrations greater than or equal to 1.0 µg/L, recoveries for most VCH by both methods were greater than 80 percent with relative standard deviations of less than 10 percent. Results from the two methods of analysis for ground-water samples collected at the site were statistically similar and indicated little apparent bias. However, only the PT-GC/MS method provided information on the individual compounds present in the aquifer.

The effect of geochemical heterogeneity in the sand and gravel aquifer on the sorption of organic compounds is discussed by Barber (1991, this Proceedings). Examination of aquifer core material indicates that minerals in the aquifer sediments differ in their ability to sorb natural and contaminant organic compounds. A relation exists between iron-bearing magnetic minerals and particle size that accounts, at least in part, for observed increases in organic sorption with decreasing particle size. In addition, sediment-bound organic carbon is not uniformly distributed throughout the aquifer, but varies as a function of space, particle size, and mineralogy.

Reverse-phase and ion-exchange chromatography, coupled with solvent extraction, were used to isolate surfactant-derived contaminants from sewage effluent and contaminated ground water at the site (Thurman and others, 1987; Field and others, 1991, this Proceedings). Spectrometric methods and GC/MS were used to identify surfactants and their biodegradation intermediates. Linear alkylbenzenesulfonates (LAS) are the most widely used surfactants in detergent formulations and they are generally considered to be biodegradable. LAS and dialkyltetralin (and dialkylindane) sulfonates (DATS) were identified in the sewage effluent and ground water 500 m from the infiltration beds. LAS half-life in the aquifer, estimated at 200 days, is an order of magnitude greater than laboratory-derived estimates. Monocarboxylated DATS and DATS biodegradation intermediates were also identified in the sewage effluent and ground water. Results indicate that alicyclic contaminants (DATS and DATS intermediates) are more persistent than their linear analogs.

Microbiology

The microbial populations and activity in the aquifer were characterized using several techniques. A method to measure microbial activity directly in the aquifer at a site where denitrification is occurring was tested using methane and a hexafluoroethane as tracers (Smith, Howes, and Garabedian, 1991). These dissolved gases were transported without retardation, but concentrations of methane apparently decreased because of biodegradation. Because the concentration of degradable dissolved organic carbon is low in the sewage plume and denitrification is consequently carbon-limited and not nitrate-limited, part of the denitrifying population appears to be autotrophic and capable of oxidizing molecular hydrogen as an alternative to carbon as an energy source (Smith and Ceazan, 1991, this Proceedings). Several strains of hydrogen-oxidizing denitrifiers have been isolated and are being characterized.

Vertical variability in the concentrations of NO_3 (nitrate), N_2 (nitrogen gas), N_2O (nitrous oxide), and the $^{15}N/^{14}N$ isotope ratios for nitrate and nitrogen gas were investigated in detail at the site (Smith, Howes, and Duff, 1991b, this Proceedings). The zone of NO_3 at the upper boundary of the sewage plume was found to be anoxic, to contain high concentrations of N_2O, and to coincide with a zone of active denitrification. Concentrations of N_2, the principal product of denitrification, are close to atmospheric equilibrium in the uncontaminated ground water, but are significantly higher in the sewage plume. Denitrification has resulted in an increase in the $^{15}N/^{14}N$ isotope ratios of both NO_3 and N_2 because of kinetic fractionation. These results demonstrate that denitrification can have a significant effect on the nitrogen geochemistry in ground water.

A series of deoxyribonucleic acid (DNA) analyses along longitudinal transects in the sewage plume shows that 85 to 99 percent of the biomass is associated with aquifer sediments (Metge and Harvey, 1991, this Proceedings). A significant part of the particle-associated DNA (up to 50 percent) is exogenous (not associated with the bacterial population on the aquifer sediments). Parts of the ground-water associated (free-living) microbial population are in the protozoan size class as determined by size fractionation of the ground water and estimated by DNA assays. Monitoring of microbial populations in the sewage plume shows that the cell numbers and DNA concentrations decrease with distance from the source of contamination.

A survey was made of the protozoan population to determine its distribution, abundance, and diversity in the sewage plume (Kinner and others, 1991, this Proceedings). Ground water and core material were examined. The use of downwell protozoa samplers to indicate the relative abundance of protozoa in the aquifer was tested. Recent evidence suggests that the protozoa samplers, which are incubated for 3 to 4 weeks within the screened sections of wells, are useful indicators of relative protozoan abundance. Two techniques have proven particularly useful in the differential enumeration of protozoa: One involves growing the organisms in nutrient media and the other involves direct enumeration by an epifluorescence technique. Large numbers (up to 100,000 per gram) of protozoa have been observed in contaminated aquifer sediments immediately downgradient from the sewage-disposal site.

A description of an injection experiment that tested the survival of a model microorganism (*Pseudomonas sp*, B13) when it was injected into contaminated ground water is presented by Krumme and others (1991, this Proceedings). A genetically altered version of this organism has been developed to biodegrade a selected organic compound. The organism was cultured, harvested, and injected at three different depths at the site. These depths represented different degrees of contamination and different oxygen concentrations. The organism survived for at least 10 weeks during this experiment and, interestingly, it survived much better in the sewage plume. Organism counts at the shallow uncontaminated depth had decreased significantly by 10 weeks.

Tracer tests conducted at two sites showed that transport of bacteria is affected by bacterial size and electrical charge on the surfaces of the bacteria (Harvey and others, 1989). In one test, the bacteria moved at the same rate as a nonreactive tracer, chloride, through about 7 m of the aquifer under a natural hydraulic gradient. Other tests included a series of small-scale forced- and natural-gradient tracer experiments using labeled bacteria at sites in contaminated and uncontaminated areas of the aquifer (Harvey and Garabedian, 1991; Harvey and others, 1991, this Proceedings). Results indicate that the magnitude of immobilization, retardation, and differential size exclusion of the bacteria from small pores can vary significantly within the aquifer. In some experiments, breakthrough patterns of bacteria closely matched that of the conservative tracers. However, earlier and later arrival (tailing) of peak microbial abundance relative to the conservative tracers has also been observed.

Chemical changes within the contaminant plume can lead to differences in reversible sorption (which controls retardation) and irreversible attachment (which controls attenuation) of bacteria. The degree of tailing in a miciobial breakthrough curve relative to that observed for a conservative tracer is indicative of reversible sorption behavior which can vary from site to site. Injection of neutralized ground water (pH 7-8) has been shown to desorb part of the labeled bacterial population sorbed to grain surfaces under acidic conditions (pH 5.5-6) during tracer tests (Harvey and others, 1991, this Proceedings).

Laboratory experiments were conducted to examine the adsorption of bacteria onto aquifer sediments under both contaminated and uncontaminated conditions (Scholl and Harvey, 1991, this Proceedings). The results indicate that in uncontaminated water the numbers of adsorbed bacteria increase with decreasing pH. However, in contaminated water there was much less response to pH changes. In addition, 2 percent of the cells were found to be reversibly adsorbed.

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 originating 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 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 with specialized sampling methods.

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DENSITY-INDUCED DOWNWARD MOVEMENT OF SOLUTES DURING A NATURAL-GRADIENT TRACER TEST, CAPE COD, MASSACHUSETTS

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ABSTRACT

Density contrasts can cause a plume of contaminated ground water to sink within an ambient flow field. Earlier studies had hypothesized that the downward movement of a bromide tracer cloud during the early part of a natural-gradient tracer test on Cape Cod, Massachusetts, was caused by density-induced sinking. Two analytical models of density-dependent flow were applied to the Cape Cod test to show that the density contrast between the ambient ground water and the tracer solution was sufficient to cause at least part of the observed sinking. The analytical models also illustrate that the amount of sinking depends on the anisotropy of hydraulic conductivity. A comparison of two- and three-dimensional analytical models for density-induced sinking indicates that downward movement predicted by the two-dimensional model is less than the downward movement predicted by the three-dimensional model of this fundamentally three-dimensional process. A numerical solute-transport model was used to show that downward movement increases with decreasing dispersion and increasing source size because both conditions serve to enhance the persistence of high concentrations in the solute cloud. The sensitivity to dispersion and the need to represent the system in three dimensions present computational difficulties for numerical simulations of density-dependent flow and solute transport.

INTRODUCTION

Vertical movement of contaminants in ground water can occur even in shallow, unconfined aquifers in which most ground water flows laterally. The movement of contaminant plumes downward because of areal recharge has been reported in several studies (Kimmel and Braids, 1980; MacFarlane and others, 1983; LeBlanc, 1984; Ryan and Kipp, 1985). The density of a contaminant plume also may cause its downward movement, even in cases where solute concentrations are well below those associated with the widely studied saltwater-intrusion problem. Kimmel and Braids (1980) suggested that dense leachate from landfills on Long Island was moving downward through ambient, uncontaminated ground water. Freyberg (1986) reported that a tracer cloud moved downward during the first part of a natural-gradient tracer test at Base Borden, Ontario, and attributed the movement to the greater density of the injected tracer solution. Van Walsun (1987) attempted to simulate the density effect observed by Freyberg (1986) with a two-dimensional numerical model, but the model predicted less sinking than had been observed during the tracer test.

This paper describes the density-induced downward movement of tracers observed during a natural-gradient tracer test that was conducted on Cape Cod, Mass. (fig. 1), in 1985-88 (LeBlanc and others, 1991) and examines the factors that affect this process by using analytical and numerical simulations. This examination is still underway, so only preliminary results are reported here.

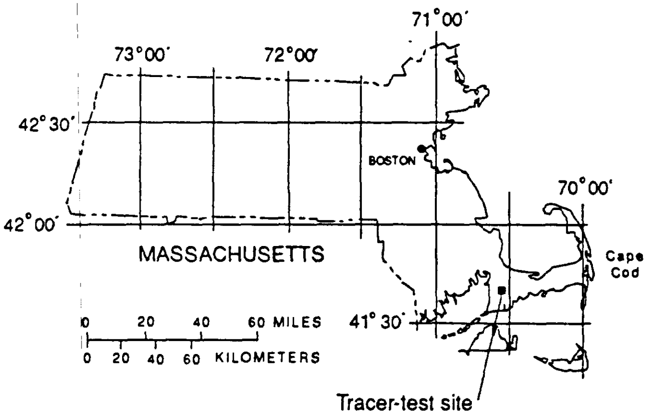

Figure 1. Location of the Cape Cod natural-gradient tracer-test site.

CAPE COD TRACER TEST

The Cape Cod natural-gradient tracer test began with the injection of 7.6 cubic meters of tracer solution into an unconfined, sand and gravel aquifer (LeBlanc and others, 1991). The solution, which was injected in three wells over a 16-hour period to approximate a pulse input, contained a nonreactive tracer, bromide, and two reactive tracers, lithium and molybdate. Movement of the tracer cloud 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 and others, 1991). The vertical position of the center of mass (one component of the first moment) clearly showed an initial period during which the tracer cloud moved downward (fig. 2). The angle of downward movement was initially as great as 3° below the horizontal. The downward movement during the first 237 days of the test was 3.2 m (meters), which is about 70 percent of the total downward movement observed during the entire 511-day experiment.

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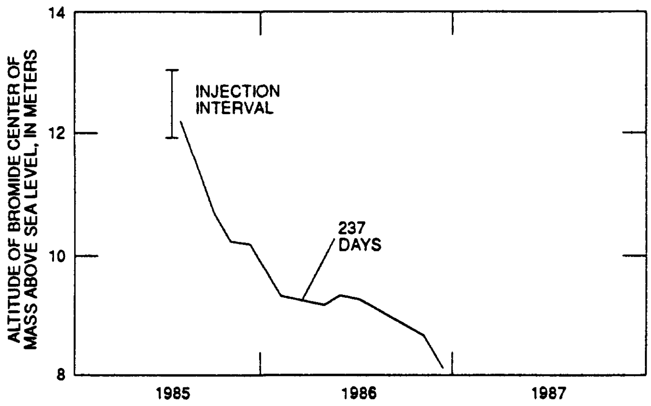

Figure 2. Vertical position of the center of mass of the bromide tracer cloud during the Cape Cod natural-gradient tracer test, 1985-87. Altitude was determined from first spatial moment in vertical direction (Garabedian and others, 1991, fig. 9).

LeBlanc and others (1991) note that vertical flow caused by accretion of areal recharge accounts 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 during the first 237 days after injection was insufficient to cause all the observed drop. They hypothesized that the additional downward movement was caused by the difference in density between the ambient ground water and the tracer solution.

The densities of the tracer solution and ambient ground water could not be determined by direct measurement because too little tracer solution was saved to allow an accurate measurement of the density contrast. Therefore, LeBlanc and others (1991) used the concentrations of dissolved solids to estimate that the density of the tracer solution was 1.00089 g/cm^3 (grams per cubic centimeter), whereas the density of the ambient ground water was 1.00004 to 1.00015 g/cm^3.

MODELING DENSITY-INDUCED VERTICAL MOVEMENT

The hypothesis that density caused the tracer cloud to sink during the Cape Cod test is being examined by use of analytical and numerical mathematical models. The ultimate objective is to simulate the observed downward movement. Work thus far has focused on determination of the sensitivity of density-induced sinking to hydrologic factors affecting solute transport.

Analytical Models

Two analytical models (Hubbert, 1953; Yih, 1965) were used to evaluate the likelihood that density was a factor in causing the observed downward movement of the tracer cloud. In the method of Hubbert (1953), the hydraulic potential of the tracer fluid is calculated in terms of the hydraulic potential of the ambient, or dominant, fluid. The direction of force acting on the tracer solution can then be determined from the gradient of its potential field. Hubbert's method, originally developed to explain the migration and entrapment of petroleum in reservoir rocks, assumes that both fluids can occupy any point in the aquifer and that the fluids do not mix. The predicted angle of downward movement for the Cape Cod tracer test, if the hydraulic conductivity is assumed to be isotropic, is 28 to 31° below the horizontal (table 1). An anisotropic conductivity tensor changes the predicted angle. For a ratio of vertical to horizontal hydraulic conductivity of 0.5 (approximately that observed at the test site), the angle reduces to 14 to 16°. Anisotropy of hydraulic conductivity affects the amount of downward movement because the direction of movement in an anisotropic aquifer is biased toward the principal direction of the hydraulic-conductivity tensor.

Table 1. *Angles of downward movement of the Cape Cod bromide tracer cloud below the horizontal as predicted by the analytical models of Hubbert (1953) and Yih (1965)*

[Tracer-solution density equals 1.00089 grams per cubic centimeter; ambient horizontal ground-water velocity is 0.42 meters per day]

	Angle of downward movement (degrees below horizontal)	
Analytical model	ρ_a[1] = 1.00004	ρ_a[1] = 1.00015
Hubbert (1953)		
K_V/K_H[2]=1.0	31.3	27.9
K_V/K_H = 0.5	15.6	13.9
K_V/K_H = 0.2	3.1	2.8
Yih (1965)		
3-D sphere	9.0	7.9
2-D infinite cylinder	6.8	5.9

[1] Ambient ground-water density, in grams per cubic centimeter.

[2] Ratio of vertical to horizontal hydraulic conductivity.

The method of Yih (1965) computes the components of velocity of a three-dimensional solute body in an ambient flow field by solving the Laplace equation with appropriate continuity and pressure conditions at the boundary between the two fluids. The method assumes that the hydraulic conductivity is isotropic and that the body, although it displaces fluid as it sinks, does not deform or become diluted by dispersion. The results do not depend on the size of the solute body. For the Cape Cod tracer test, the predicted angle of downward movement of a spherical body is 8 to 9° below the horizontal. This angle is smaller than that predicted by the Hubbert (1953) method because the method of Yih (1965) accounts for energy losses associated with the displacement of ambient ground water by the sinking tracer cloud.

Reduction of the Yih (1965) solution to two dimensions (an infinitely long circular cylinder, or a circle in the two-dimensional plane) results in a predicted downward angle about 25 percent smaller than that obtained from the three-dimensional analysis (table 1). In the two-dimensional model, all displacement of water must occur parallel to the section, whereas displacement occurs in all directions in the real, three-dimensional system. Therefore, 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. This limitation would also apply to two-dimensional numerical models and may help explain why Van Walsun (1987) was unable to reproduce the observed downward movement of tracers during the Borden experiment with a two-dimensional model without using a large density contrast and a large ambient vertical hydraulic gradient.

During the Cape Cod tracer test, the density contrast between the ambient ground water and the tracer cloud decreased as the tracer cloud was diluted by dispersion (LeBlanc and others, 1991, table 3). The decreasing density would be expected to cause a gradual decrease of the angle of downward movement, which, in turn, would result in a parabolic trajectory of the center of mass similar to that observed during the test (fig. 2). Because this gradual decrease in density is not accounted for in the models of Hubbert (1953) and Yih (1965), these models tend to predict a greater rate of sinking than would be predicted in models that include the effect of dispersion.

Numerical Model

The results obtained from the analytical models were extended by using numerical simulations to examine density-induced sinking when solute concentrations and density are allowed to decrease because of dispersion. SUTRA (Voss, 1984), a two-dimensional finite-element model that simulates solute tranport and dispersion in a density-dependent flow field, was used for these simulations. The numerical simulations 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 Simulations

For the simulations reported here, SUTRA was used to simulate a transport problem similar to the Cape Cod tracer test. This simplification was acceptable because the purpose of these preliminary simulations was to examine the factors that affect density-induced sinking, not to match the sinking observed during the Cape Cod test. Accurate simulations of the field test are the goal of the next phase of work.

The grid, a two-dimensional vertical section, encompassed an area 2.5 m high and 15 m long. This area was subdivided into 3,750 elements. Because longitudinal and transverse dispersivities as small as 0.05 and 0.005 m, respectively, were used in the models, each element was only 0.2 m long and 0.05 m high. With this fine grid spacing, the Peclet number was less than 4 and the transverse spacing was less than 10 times the transverse dispersivity (Voss, 1984, p. 232-233).

Aquifer characteristics were similar to those reported for the Cape Cod tracer-test site (LeBlanc and others, 1991). An ambient, steady, horizontal velocity of 0.45 m/d (meters per day) was established by specifying a hydraulic conductivity of 120 m/d, a porosity of 0.39, and appropriate pressures along the left and right boundaries of the model. Hydraulic conductivity was assumed to be isotropic, although planned work will include simulations in which it will be anisotropic. The top and bottom of the model were specified as zero-flux boundaries.

Most simulations began with the instantaneous release of a solute cloud that covered an area 0.5 m high and 2.0 m long (fig. 3). The solute cloud was simulated for 10 days (40 time steps). A small time step of 0.25 days was needed to minimize numerical dispersion (Voss, 1984, p. 234). Each simulation took about 3 hours of CPU time on a PR1ME[3] 9955 computer.

The movement of the simulated tracer cloud was displayed by means of contoured plots of calculated concentrations generated using a plotting program developed by Souza (1987). Spatial moments of the simulated concentration distributions were calculated by numerical integration of concentrations using bilinear interpolation across the model elements.

Simulated Movement of the Tracer Cloud

The simulated tracer cloud moved downward because of the density difference between the ambient ground water and the tracer solution. A series of simulations confirmed that the downward component of movement is sensitive to the initial density difference. This downward movement is evident in the results of a typical simulation shown in figure 3. For this simulation, a large initial source concentration was used to increase the density-induced sinking; the initial tracer-cloud density was about four times greater than that in the actual tracer test. The tracer cloud develops a saddle shape as the cloud disperses while being tranported (fig. 3). This shape develops because the center of the cloud, where concentrations are highest and the downward forces caused by density are strongest, moves downward more rapidly than do the edges of the cloud, where concentrations are diluted by dispersion and the downward forces are weaker.

The downward movement also affects directions of flow in the ambient fluid as it is displaced by the sinking tracer cloud. Although the largest downward component of flow coincided with the highest concentration and greatest density in the tracer cloud, the largest upward component of flow was immediately behind and above the cloud where ambient water moves to fill the area left by the downward moving cloud. As the initial density contrast is increased, the disturbance of the velocity field increases and the saddle shape of the cloud becomes more pronounced.

The downward component is also very sensitive to the rate at which concentrations in the cloud are diluted by dispersion. Even a small amount of dispersion can quickly decrease maximum concentrations and limit the amount of vertical movement. This effect is shown in figure 4 for a set of simulations in which source size and initial densities of the ambient fluid and tracer solution (equal to those of the Cape Cod test) were held constant, but the longitudinal

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[3] The use of brand names in this paper is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

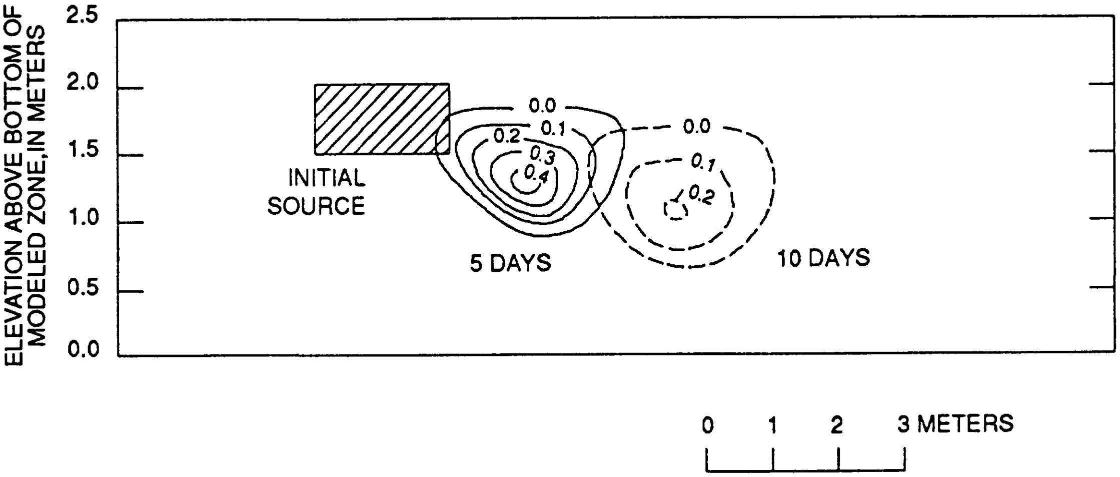

Figure 3. Vertical section showing simulated position of tracer cloud at 5 and 10 days after start of simulation. Contour interval 0.1 relative concentration (ratio of simulated to initial concentration). Longitudinal and transverse dispersivities are 0.11 and 0.005 meters, respectively.

dispersivity was varied from 0.11 to 1.01 m. The effects of dispersion are also related to source size. High concentrations persist longer in large clouds than in small clouds, so the centers of mass of large clouds tend to sink more than those of small clouds of the same initial density.

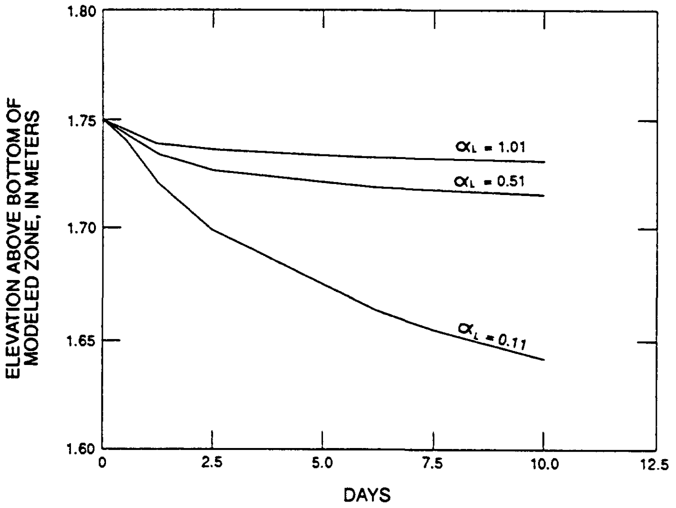

Figure 4. Vertical position of the center of mass of the simulated tracer cloud during a 10-day-long period for longitudinal dispersivities of 0.11, 0.51, and 1.01 meters. Transverse dispersivity was 0.005 meters.

DISCUSSION

The analytical models of Hubbert (1953) and Yih (1965) were used to show that the density difference between the ambient ground water and the tracer solution for the Cape Cod test was sufficient to cause part of the observed downward movement of the tracer cloud. However, their usefulness in predicting the amount of sinking is limited because neither approach accounts for the critical effect of dispersion.

The numerical modeling clearly indicates that dispersion and source size greatly affect density-induced sinking. Field experiments (Freyberg, 1986; Garabedian and others, 1991) and stochastic transport theory (Dagan, 1984) indicate that field-scale dispersion is initially very small but increases to an asymptotic limit as the solute cloud travels through the heterogeneous aquifer. The numerical simulations suggest that this initially small dispersivity limits dilution that would otherwise rapidly diminish the density-induced downward movement. The consequence is that numerical models must use very small initial dispersivities to simulate density-induced sinking accurately. Van Walsun (1987) reported that the trajectory of the Borden tracer cloud was best simulated in a two-dimensional model when a very small initial dispersivity was used that increased with time. This requirement greatly increases the number of grid cells needed near the source. Accurate modeling may also require simulation of three-dimensional flow. Both requirements add significantly to the computational effort.

SUMMARY

Downward movement of the center of mass of the solute cloud was observed during the first 237 days of the Cape Cod tracer test. Earlier studies had hypothesized that this sinking was caused in part by the density difference between the ambient ground water and the injected tracer solution.

Two analytical models of density-dependent flow were used to demonstrate that the density contrast during the Cape Cod test was sufficient to cause part of the observed sinking. Application of the Hubbert model showed that the extent of sinking depends on the anisotropy of hydraulic conductivity, whereas application of the Yih model showed that the tendency to move downward is balanced, in part, by the displacement of water around the sinking tracer cloud. The Yih model also suggested that less sinking is predicted in two-dimensional models than in three-dimensional models of this fundamentally three-dimensional process.

The SUTRA numerical model was used to illustrate that the amount of downward movement is related to dispersion and source size because both factors affect the persistence of high concentrations in the center of the solute cloud. The sensitivity to dispersion and the need to represent the system three-dimensionally present computational challenges when simulating this type of process with numerical models.

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ESTIMATION OF MACRODISPERSIVITIES FROM THE SPATIAL VARIABILITY OF HYDRAULIC CONDUCTIVITY IN A SAND AND GRAVEL AQUIFER, CAPE COD, MASSACHUSETTS

By Kathryn M. Hess[1], Steven H. Wolf[2], *and* Michael A. Celia[3]

ABSTRACT

Spatial variability of hydraulic conductivity in a sand and gravel aquifer on Cape Cod, Massachusetts, was investigated in order to test stochastic transport equations relating macrodispersion to the statistical properties of the hydraulic-conductivity distribution. Nearly 1,500 measurements of hydraulic conductivity were obtained by borehole-flowmeter tests and permeameter analyses of cores. The geometric mean hydraulic conductivity from the flowmeter tests is 0.11 centimeters per second--a rate similar to that estimated from a tracer test conducted at this site and an aquifer test conducted nearby. The geometric mean from the permeameter tests is 0.035 centimeters per second. This significantly lower value may result from compaction of the cores, nonrepresentative sampling, anisotropy of hydraulic conductivity, or a difference in averaging volumes between the two methods. The variance of the log-transformed hydraulic conductivity is also greater for the flowmeter values (0.24) than for the permeameter values (0.14). Geostatistical analysis of the hydraulic conductivities from the two methods reveals similar spatial-correlation structures; neither method detected any horizontal anisotropy. Isotropic horizontal correlation scales from variogram models with and without a nugget effect range from 2.9 to 8.0 meters; vertical correlation scales range from 0.18 to 0.38 meters. A ratio of vertical to horizontal effective hydraulic conductivity of 1:1.2 is estimated by stochastic analysis. This ratio is slightly greater than previously reported ratios for the aquifer. Stochastic transport equations were also used to estimate asymptotic longitudinal macrodispersivities; these values, 0.35 to 0.78 meters, are similar to the longitudinal dispersivity of 0.96 meters observed in the tracer test. The predicted early-time development of the dispersion process indicates that a constant longitudinal dispersivity is reached quickly as was observed in the tracer test. The transport theories estimate that longitudinal dispersivity exceeds the transverse components, as was observed in the tracer test. However, the predicted transverse dispersivities (10^{-6} to 10^{-7} meters) are lower than those observed in the tracer test (0.018 and 0.0015 meters for the transverse horizontal and transverse vertical dispersivities respectively). Incorporation of unsteady flow conditions increases the predicted value of transverse horizontal dispersivity to 0.025 meters.

INTRODUCTION

Macrodispersion is the hydrodynamic spreading of solutes in a porous medium caused by a variable flow field which, in turn, is caused by the heterogeneity characteristic of aquifers. Several stochastic transport equations have been proposed that relate macrodispersion to the variability of aquifer properties, particularly hydraulic conductivity (Gelhar and Axness, 1983; Dagan, 1984). These equations have been tested only to a limited degree by comparing estimates of macrodispersivity from field tracer tests to estimates obtained by application of the stochastic equations to field measurements of hydraulic conductivity. The experiments of this type conducted in a sandy aquifer at Base Borden, Ontario (Freyberg, 1986; Sudicky, 1986), generally supported the validity of the stochastic approach.

The link between macrodispersion and aquifer heterogeneity is being investigated in an unconsolidated, unconfined aquifer on Cape Cod, Mass. A natural-gradient tracer test was conducted at the Cape Cod site in which the transport of bromide, a nonreactive, conservative tracer, was monitored for 2 years in the medium to coarse sand and gravel aquifer (LeBlanc and others, 1991). From an analyses of spatial moments of the distribution of bromide in the aquifer, a dispersivity tensor was calculated for the transport of the tracer (Garabedian and others, in 1991). The stochastic transport equations developed by Gelhar and Axness (1983), Dagan (1984) and Rehfeldt (1988) were then used in conjunction with a statistical analysis of hydraulic-conductivity data measured at the Cape Cod site to estimate macrodispersion for the aquifer. This paper describes the estimation of macrodispersivities at the Cape Cod site by the stochastic approach and compares these estimates to the macrodispersivities obtained from the tracer test.

METHODS OF MEASURING HYDRAULIC CONDUCTIVITY

Two methods were used to determine hydraulic conductivity over small intervals of the aquifer: *in-situ* borehole-flowmeter tests (Hess, 1989) and laboratory, multiport permeameter tests of intact cores (Wolf, 1988; Wolf and others, 1991). The vertical interval of the aquifer over which flowmeter and permeameter measurements were made, a 6- to 7.5-m (meter) interval just below the water table, was the same as that through which the bromide tracer traveled in the natural-gradient tracer test. However, the flowmeter wells and coring sites were located about 25 m west of the tracer-test site (fig. 1) to preserve the site for future tracer tests. For the most part, flowmeter and permeameter measurements were made in different holes because the auger drilling method used in the coring procedure significantly disturbs the surrounding aquifer (Morin and others, 1988). Drive-and-wash drilling, a less disruptive method, was used to install most flowmeter wells so that the aquifer disturbance would be minimized for these *in-situ*, hydraulic tests.

Borehole-flowmeter tests were conducted in 5-cm-(centimeter)-diameter wells which were screened over a 12-m interval just below the water table. Lateral distances between the 16 wells ranged from 1 to 22 m (fig. 1).

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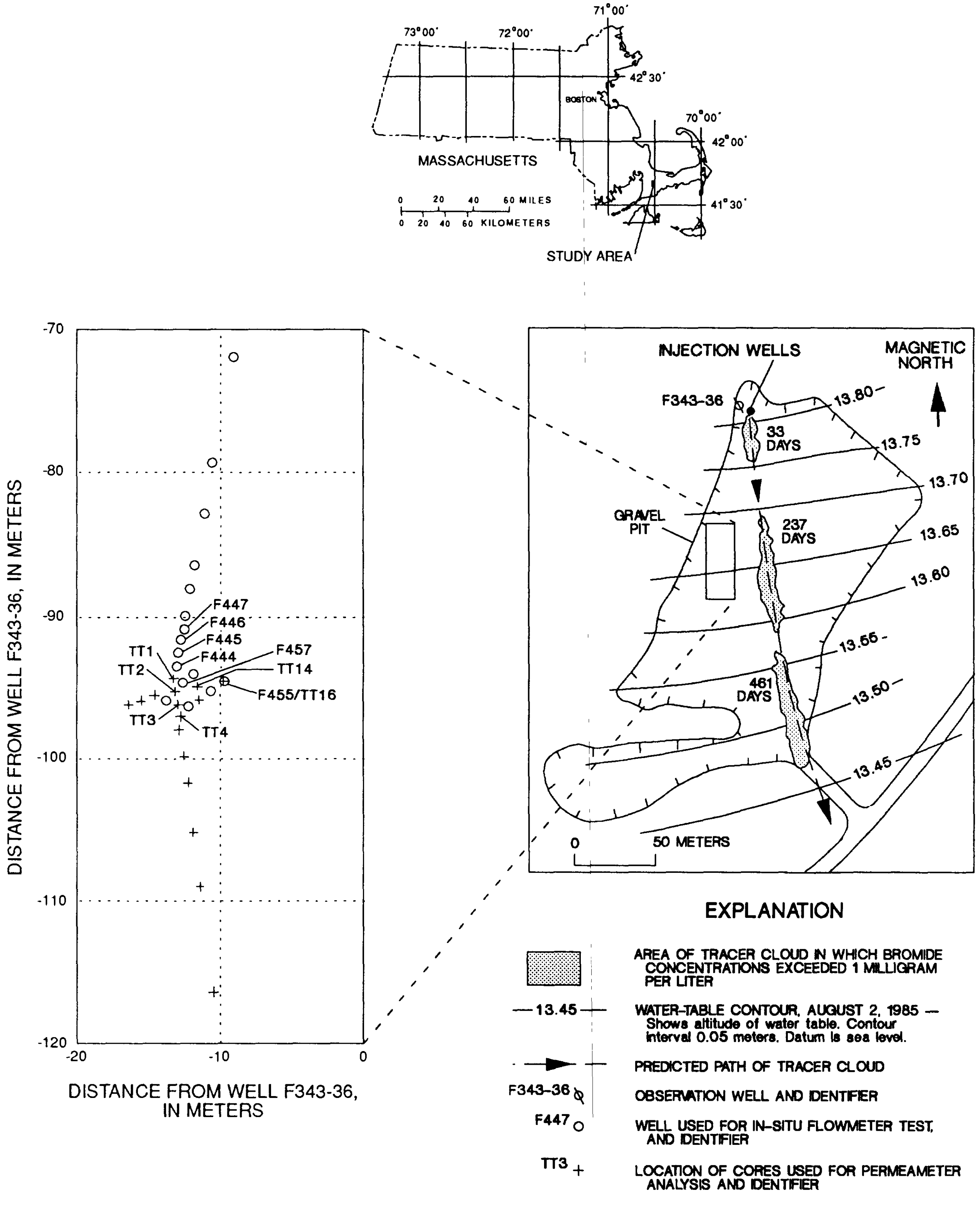

71°00'
73°00'
72°00'
42°30'
BOSTON
70°00'
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MASSACHUSETTS
41°30'
0 20 40 60 MILES
0 20 40 60 KILOMETERS
STUDY AREA
-70
-80
-90
-100
-110
-120
-20
-10
0
DISTANCE FROM WELL F343-36, IN METERS
DISTANCE FROM WELL F343-36, IN METERS
F447
F446
F445
F444
F457
TT14
F455/TT16
TT1
TT2
TT3
TT4
INJECTION WELLS
MAGNETIC NORTH
F343-36
13.80
13.75
13.70
13.65
13.60
13.55
13.50
13.45
33 DAYS
237 DAYS
461 DAYS
GRAVEL PIT
0
50 METERS
EXPLANATION
AREA OF TRACER CLOUD IN WHICH BROMIDE CONCENTRATIONS EXCEEDED 1 MILLIGRAM PER LITER
13.45 WATER-TABLE CONTOUR, AUGUST 2, 1985 — Shows altitude of water table. Contour interval 0.05 meters. Datum is sea level.
PREDICTED PATH OF TRACER CLOUD
F343-36 OBSERVATION WELL AND IDENTIFIER
F447 WELL USED FOR IN-SITU FLOWMETER TEST, AND IDENTIFIER
TT3 LOCATION OF CORES USED FOR PERMEAMETER ANALYSIS AND IDENTIFIER

Figure 1. Tracer-test site in abandoned gravel pit, showing water-table contours, observed path of nonreactive bromide tracer cloud, injection wells, reference monitoring well F343-36, wells for flowmeter tests, and coring sites. Path of tracer cloud from LeBlanc and others (1991, fig. 4).

The flowmeter tests were based on the method developed by Hufschmied (1986) and modified by Rehfeldt and others (1989). This procedure involves measuring the incremental increase in discharge up the well with a highly sensitive, impeller flowmeter, while maintaining a nearly constant drawdown in the well by pumping near the water table. This method is analogous to a standard aquifer test except that discharge is measured at short intervals along the screen, instead of only at the wellhead. Hydraulic conductivity for each interval is then calculated from these field measurements. A total of 668 estimates of hydraulic conductivity over vertical intervals of 15 cm were used in the statistical analysis reported below.

Multiport, constant-head permeameter measurements were conducted on relatively undisturbed, 5-cm-diameter cores obtained using the coring method of Zapico and others (1987). The 16 boreholes were interspersed among the flowmeter wells. Lateral distances between boreholes ranged from 1 to 22 m (fig. 1). Radiographs of the cores were used to identify intervals of similar structure or inferred grain size over which to make the permeameter measurements. Intervals which contained large gravel particles, as determined by visual inspection of the radiographs, were not included because the large particles obstruct flow in the permeameter. The liners in which the cores were collected served as the permeameter body into which manometer probes were inserted between the identified intervals. Hydraulic conductivities were calculated from permeameter tests on 825 vertical core intervals that averaged 7.3 cm in length.

RESULTS OF FLOWMETER AND PERMEAMETER TESTS

Both methods produced detailed profiles of hydraulic conductivity within the aquifer. Figure 2 presents four profiles obtained by each method from the central cluster (fig. 1) where wells or coring locations are separated by only one meter from their nearest neighbor. A high degree of variability is evident in the vertical direction for both types of hydraulic-conductivity measurements. Much more continuity is observed in the horizontal direction; several zones of similar hydraulic conductivity are horizontally continuous across the entire area investigated. From these qualitative observations, the horizontal correlation scale of the hydraulic-conductivity distribution was expected to be much greater than the vertical correlation scale.

The flowmeter method yielded a geometric mean hydraulic conductivity of 0.11 cm/s (centimeters per second), which is similar to the mean of 0.13 cm/s estimated from a nearby aquifer test (LeBlanc and others, 1988) and from the tracer test (LeBlanc and others, 1991). In contrast, the geometric mean of the permeameter values is ony 0.035 cm/s. The permeameter tests were run on vertical cores and, therefore, were measuring vertical hydraulic conductivities. The ratio of the permeameter mean (measured vertically) to flowmeter mean (measured horizontally) of 1:3 is within the range of vertical to horizontal anisotropy of 1:2 to 1:5 previously reported for this aquifer (LeBlanc and others, 1988). This implies that anisotropy is partly responsible for the difference in means. However, it was hypothesized that hydraulic conductivity is isotropic at the scale over which permeameter measurements were made (5 - 10 cm) and that the permeameter tests would yield valid estimates of the horizontal hydraulic conductivity. Repacking experiments (Wolf, 1988) seemed to support this hypothesis. Other possible explanations for the difference in means between the methods include nonrepresentative sampling of the aquifer by the cores, loss of porosity in the cores by compaction, and differences in the sampling volumes of the two methods.

The variances of the natural logarithm of hydraulic conductivity also differ between the two measurement techniques. The flowmeter variance of 0.24 is significantly higher than the permeameter variance of 0.14, even though the averaging interval of 7.3 cm for the permeameter measurements is half of the 15-cm interval of the flowmeter tests and, therefore, the permeameter measurements might be expected to result in a greater variance.

GEOSTATISTICAL ANALYSIS

To obtain estimates of the correlation structure, a geostatistical analysis (Journel and Huijbregts, 1978) of the spatial variability of hydraulic conductivity was performed on the flowmeter and permeameter data. The resulting variograms in the vertical direction for the flowmeter and permeameter data are shown in figure 3. Estimates of the correlation scales were obtained by fitting a negative exponential model to the experimental variograms by minimizing the sum of squares and using sill values that were similar to the sample variances. A visual check was also conducted and, in some cases, the correlation scale and sill value were adjusted slightly to provide a better fit between the rising limb of the model and the experimental variogram. The estimated vertical correlation scales are 0.19 and 0.18 m for the flowmeter and permeameter data, respectively (fig. 3A and 3B).

No statistically significant horizontal anisotropy was observed in a directional analysis of the data sets, possibly because most of the flowmeter wells and core sites are located along a north-south-oriented transect (fig. 1). Consequently, horizontal variograms (fig. 4) were constructed assuming isotropy in the horizontal direction. These variograms display a possible "nugget effect" (Journel and Huijbregts, 1978); thus, negative-exponential models with and without nugget values were fit to the experimental variograms. The nugget value possibly represents a measurement-error effect or a correlation structure at a scale smaller than the scale over which measurements were made. The resulting horizontal correlation scales range from 2.9 to 8.0 m, but the values from the permeameter data are consistently less than the values from the flowmeter data (fig. 4). Corresponding nugget models also were fit to the vertical variograms and the resulting correlation scales are 0.38 and 0.35 m for the flowmeter and permeameter data, respectively (fig. 3C and 3D).

MACRODISPERSION ESTIMATES

Asymptotic macrodispersivities were estimated using the stochastic transport equations of Gelhar and Axness (1983) with the ranges of variances and correlation scales determined in the geostatistical analysis of the hydraulic-conductivity distribution (figs. 3 and 4). Because no horizontal anisotropy of hydraulic conductivity was observed, isotropy in the plane of stratification was assumed (Gelhar and Axness, 1983, Case 1). The longitudinal-dispersivity

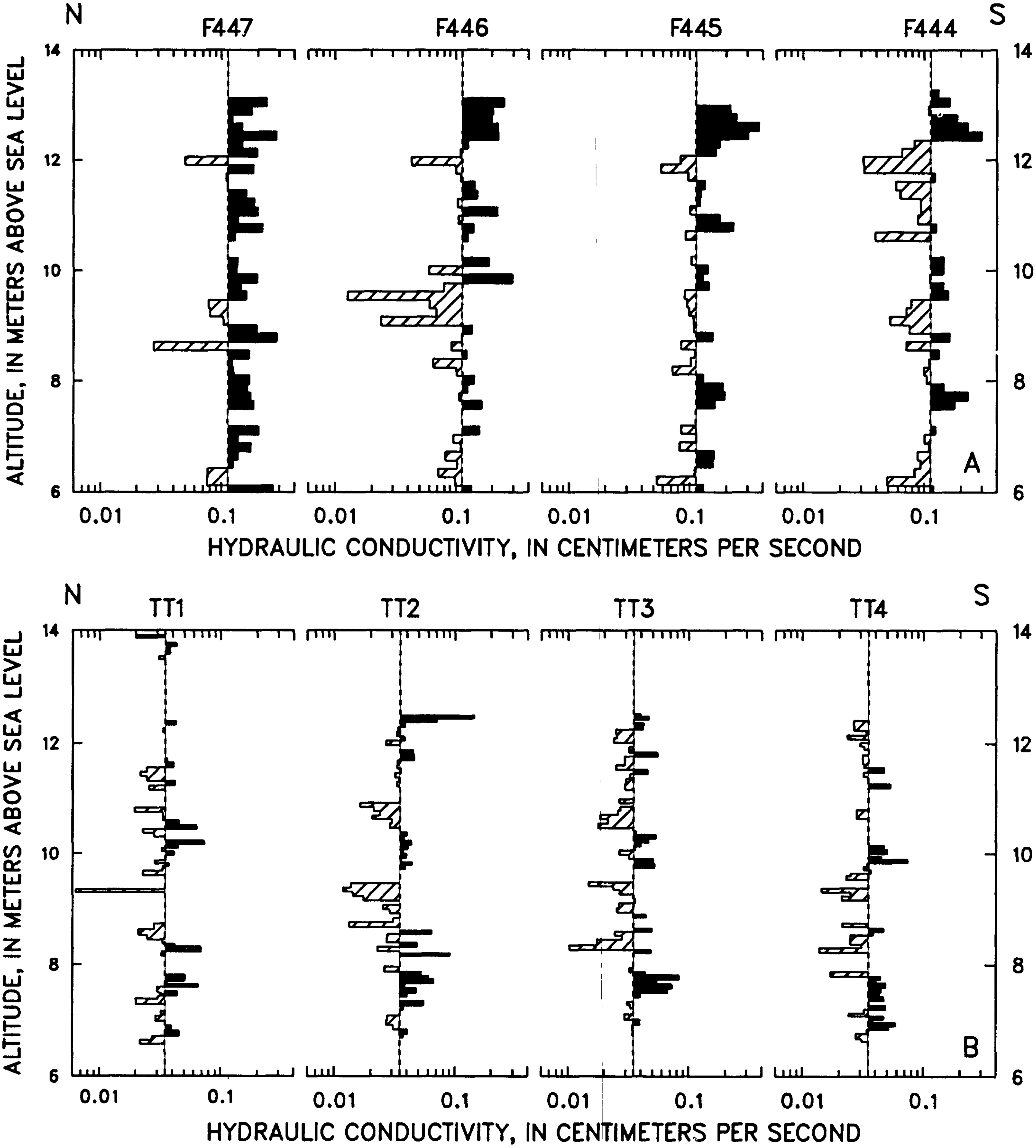

Figure 2. Hydraulic-conductivity profiles from (A) flowmeter tests and (B) permeameter analyses at locations in central cluster where sampling sites are separated by approximately 1 meter. Locations shown in figure 1. Dotted lines indicate the geometric mean hydraulic-conductivity value for each method. Solid shading indicates zones of hydraulic conductivity greater than the geometric mean. Slanted-line shading indicates zones less than the geometric mean.

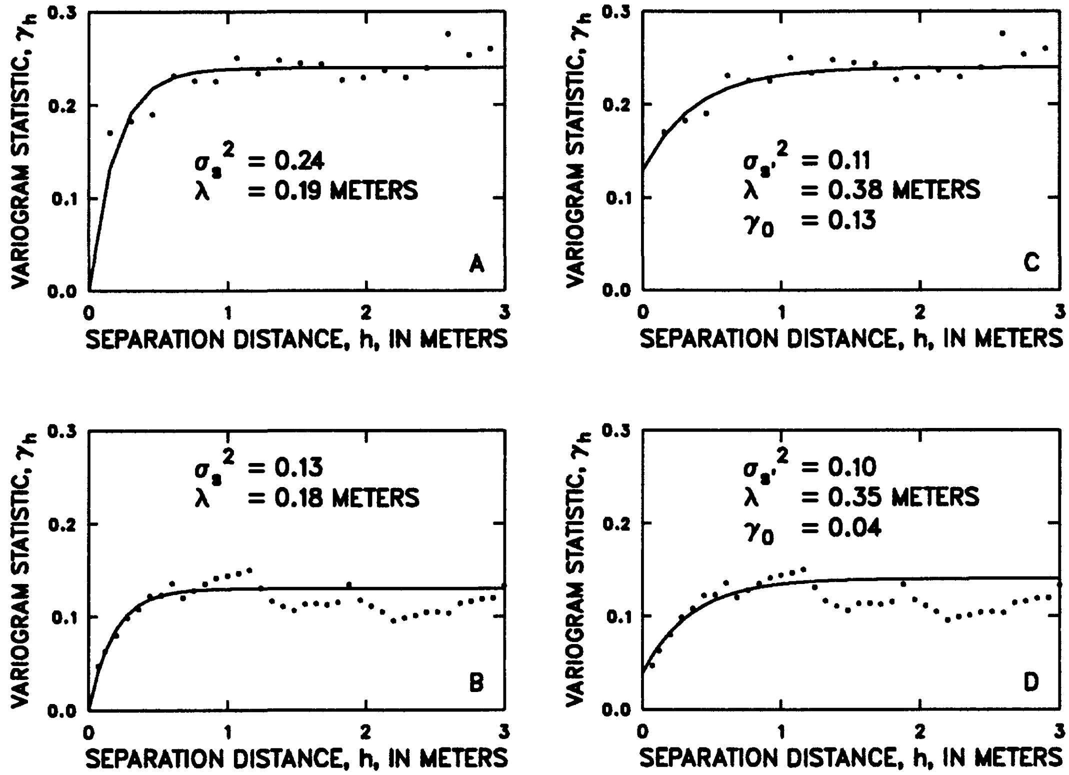

Figure 3. Vertical variograms of natural-logarithm of hydraulic conductivity. Exponential models of the form $\gamma_h = \sigma_s^2(1 - \exp(-h/\lambda))$ are fit to the experimental variograms from (A) flowmeter and (B) permeameter data, where γ_h = the variogram statistic, σ_s^2 = the sill value, h = the separation distance, and λ = the correlation scale. Nugget-exponential models of the form $\gamma_h = \gamma_0 + \sigma_s'^2(1 - \exp(-h/\lambda))$ are fit to the experimental variograms from (C) flowmeter and (D) permeameter data, where γ_0 = the nugget part of the sill value, and $\sigma_s'^2$ = the remaining part of the sill value.

estimates range from 0.35 to 0.78 m. This range is similar to the longitudinal dispersivity of 0.96 m observed in the tracer test (Garabedian and others, 1991).

Application of the stochastic equations of Gelhar and Axness (1983) also indicates that longitudinal dispersivity exceeds the transverse components, as was observed in the tracer test. The estimated transverse components were only 10^{-6} to 10^{-7} m, whereas the transverse horizontal and vertical dispersivities from the tracer test were 0.018 and 0.0015 m, respectively (Garabedian and others, 1991). Changes in the direction of the hydraulic gradient during the tracer test may have caused significant lateral mixing and, thus, enhanced the transverse horizontal dispersion observed in the tracer test. The estimate of transverse horizontal dispersivity from the transport theory increases to 0.025 m when the effects of a transient flow field are incorporated using Rehfeldt's (1988) modification of the theory of Gelhar and Axness (1983). The transient flow field has no effect on the longitudinal-dispersivity estimates because horizontal isotropy was assumed.

The stochastic theory developed by Dagan (1984) was used to predict the time rate of change of the variances of the concentration distribution from the statistical properties of the hydraulic-conductivity distribution (fig. 5) and, thus, to investigate the early-time dispersion process when dispersivities increase with travel distance (or time). When dispersivities are constant, the time rate of change of the variances is constant. The theory predicted that a constant time rate of change and, thus, a constant longitudinal dispersivity, was reached quickly, as was observed in the tracer test (Garabedian and others, 1991). However, the predicted graph of changes in longitudinal variance with time did not match the observed trend (fig. 5A). Similarly, the predicted early-time change of the transverse horizontal variance (fig. 5B) did not match the observed change.

EFFECTIVE HYDRAULIC CONDUCTIVITY

The stochastic transport equations of Gelhar and Axness (1983) also were used to estimate the anisotropy of the effective hydraulic-conductivity tensor from the flowmeter and permeameter data. The ratio of vertical to horizontal hydraulic conductivity was estimated to be 1:1.2, which is reasonable for this type of sand and gravel aquifer, but is slightly greater than the ratio of 1:2 to 1:5 from a nearby aquifer test (LeBlanc and others, 1988).

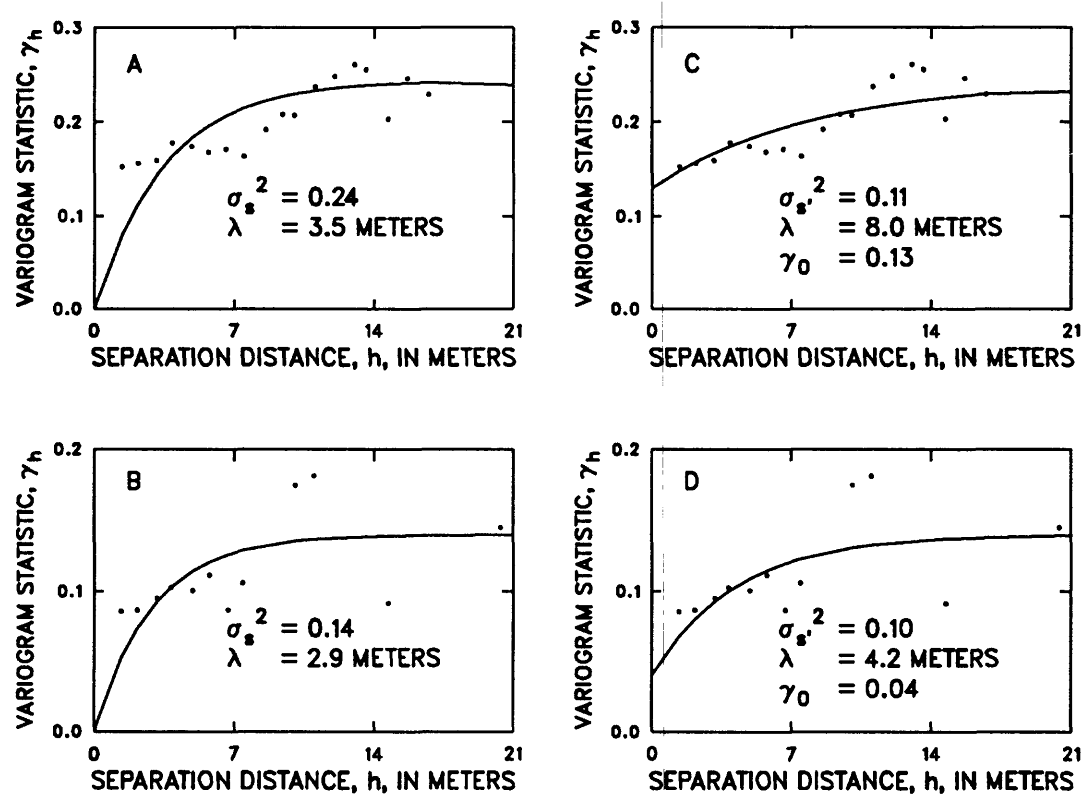

Figure 4. Isotropic horizontal variograms of natural-logarithm of hydraulic conductivity. Exponential models of the form $\gamma_h = \sigma_s^2(1 - \exp(-h/\lambda))$ are fit to the experimental variograms from (A) flowmeter and (B) permeameter data, where γ_h = the variogram statistic, σ_s^2 = the sill value, h = the separation distance, and λ = the correlation scale. Nugget-exponential models of the form $\gamma_h = \gamma_0 + \sigma_s'^2(1 - \exp(-h/\lambda))$ are fit to the experimental variograms from (C) flowmeter and (D) permeameter data, where γ_0 = the nugget part of the sill value, and $\sigma_s'^2$ = the remaining part of the sill value.

CONCLUSIONS

Flowmeter tests in long-screened wells provided an accurate method for assessing small-scale variability in hydraulic conductivity at the Cape Cod site; the resulting geometric mean of hydraulic conductivity is similar to the mean obtained from the tracer test and an aquifer test. The permeameter method yielded a mean hydraulic conductivity that is less than that determined by the flowmeter and other methods. The lower mean could be caused by nonrepresentative sampling, loss of porosity in the samples, anisotropy of hydraulic conductivity, and a difference in averaging volume between the two methods. The variances are also greater for the flowmeter values than for the permeameter values. Similar correlation structures were obtained from geostatistical analyses of the flowmeter and permeameter data. The ratio of vertical to horizontal effective hydraulic conductivity resulting from the stochastic equations is slightly greater than the ratio calculated from a nearby aquifer test. Horizontal anisotropy of hydraulic conductivity was not observed, so isotropy in the plane of stratification was assumed in the macrodispersivity calculations. Stochastic transport equations were used to predict a range of asymptotic longitudinal dispersivities from the statistical description of the hydraulic-conductivity variability; this range is similar to the value obtained from the tracer test. Transverse horizontal and transverse vertical dispersivities were underestimated by the equations, probably because the equations do not take into account transient-flow effects. Modified stochastic equations that incorporate the effects of lateral changes in the hydraulic-gradient direction yielded a transverse horizontal dispersivity that was similar to that obtained from the tracer test. Early-time changes in variance with travel time, estimated from the hydraulic-conductivity distribution indicate that a constant longitudinal dispersivity is reached quickly in this aquifer, as was observed in the tracer test.

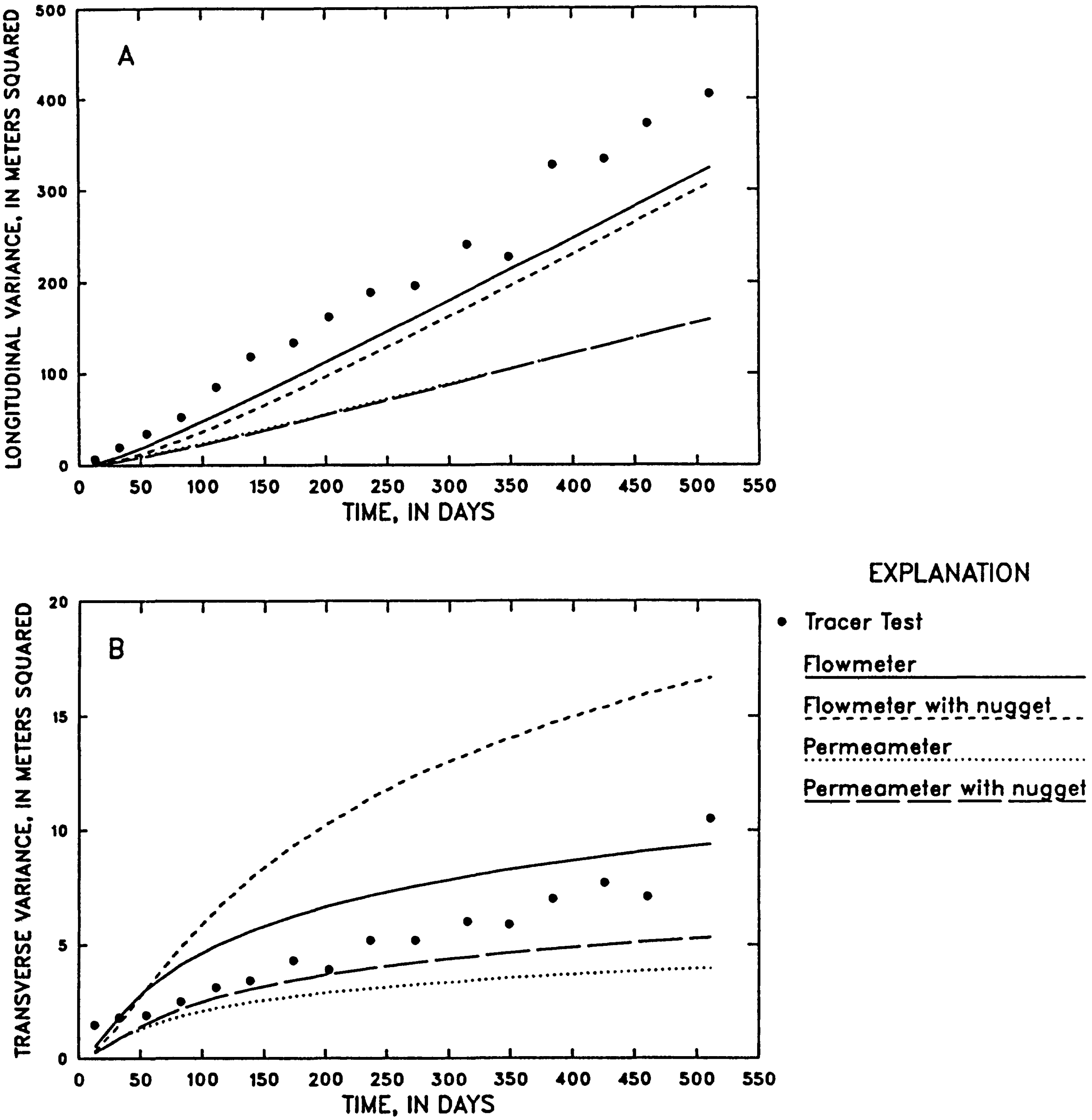

Figure 5. Time rate of change of (A) longitudinal and (B) transverse variance of concentration as observed in the tracer test (Garabedian and others, 1991) and as predicted from Dagan (1984) using the flowmeter and permeameter hydraulic-conductivity results.

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PRELIMINARY DETERMINATION OF HYDRAULIC CONDUCTIVITY IN A SAND AND GRAVEL AQUIFER, CAPE COD, MASSACHUSETTS, FROM ANALYSIS OF NUCLEAR LOGS

By Roger H. Morin[1] *and* Kathryn M. Hess[2]

ABSTRACT

An algorithm was developed to predict hydraulic conductivity from nuclear logs for a sand and gravel aquifer on Cape Cod, Massachusetts. Flowmeter tests conducted in long-screened wells at the site provided detailed vertical profiles of horizontal hydraulic conductivity, and nuclear logs provided quantitative estimates of porosity (neutron log) and qualitative indications of grain size (natural-gamma log) for 0.15-meter vertical sections of the aquifer. Because grain-size data were not available to develop a direct relation between grain size and gamma activity, hydraulic conductivities from the flowmeter tests and porosities from neutron logs were substituted into the Kozeny-Carmen equation to obtain estimates of grain size for three wells. A logarithmic relation between the square of the grain-size estimates and the gamma response was then developed. Representative values of grain size predicted by this relation and porosities obtained from neutron logs were then used to compute a vertical profile of hydraulic conductivity for a well that was not used to develop the algorithm. A comparison of predicted and observed hydraulic conductivities indicates that this preliminary algorithm was unable to reproduce the hydraulic conductivity profile accurately and needs to be refined. However, the algorithm did predict a hydraulic-conductivity distribution with a mean, variance, and vertical correlation scale similar to those of the observed distribution and, thus, may be useful in providing input parameters for the stochastic analysis of solute transport in the aquifer.

INTRODUCTION

Results from flowmeter-hydraulic tests conducted in wells at the Cape Cod Toxic-Substances Hydrology Research Site (fig. 1) comprise a comprehensive data base with which the spatial distribution of hydraulic conductivity of a sand and gravel aquifer was examined (Hess, 1989). These detailed measurements also provide the opportunity to evaluate alternative methods of estimating hydraulic conductivity and its variability. The purpose of this investigation was to use nuclear logs obtained from these wells to develop an algorithm that would predict hydraulic conductivities at this site.

In general, geophysical-logging activities do not impose a hydraulic stress or disturbance upon the surrounding aquifer, and do not directly measure hydraulic conductivity. However, the epithermal-neutron and natural-gamma logs record lithologic changes and provide information on aquifer heterogeneity (Keys, 1988). These two nuclear logs, combined with flowmeter measurements, were used to develop a preliminary algorithm based on a relation between hydraulic conductivity and porosity and grain-size distributions. This algorithm yields indirect estimates of hydraulic conductivity for the aquifer from nuclear logs. In this paper, predicted values of hydraulic conductivity are compared with direct measurements and statistical parameters associated with their spatial distributions are evaluated.

FIELD METHODS

The four wells used in the development and preliminary assessment of the method are part of a 22-m-(meter)-long transect of 10 wells (fig. 1) that is approximately parallel to the mean direction of ground-water flow. The wells were installed as part of an investigation of the distribution of horizontal hydraulic conductivity in this sand and gravel aquifer (Hess, 1989). The wells were cased with 5-centimeter-diameter, flush-jointed, threaded polyvinyl chloride (PVC) and screened over a 12-m interval below the water table. The wells were installed by a drive-and-wash technique that minimizes disturbance of the formation around the wells (Morin and others, 1988).

A spinner-flowmeter log was obtained in each of these wells during pumping, and the resulting data were used to determine the vertical distribution of horizontal hydraulic conductivity by the method developed by Hufschmied (1986) and Rehfeldt and others (1989). The vertical measurement interval and, correspondingly, the minimum scale of investigation of the aquifer were 0.15 m. Thus, these measurements defined high-resolution profiles of horizontal hydraulic conductivity for each of the 10 wells.

Epithermal-neutron and natural-gamma logs also were collected in the 10 wells. These logs are not adversely affected by the PVC well-casings. Sampling frequency, digitizing rates, and logging speed were selected such that values of neutron absorption and natural-gamma activity directly corresponded in space to a value of hydraulic conductivity determined from the flowmeter tests. Thus, gamma and neutron response, in units of counts per second (cps), and horizontal hydraulic conductivity were obtained in each well for each 0.15-m vertical interval of the screened section of the aquifer.

The natural-gamma log is a measure of gamma radiation emitted by the surrounding formation. Clays tend to accumulate radionuclides through adsorption and ion-exchange processes, and the gamma activity associated with clay-bearing sediments typically is greater than that of other siliceous and calcareous deposits. Consequently, zones of high gamma activity routinely are classified as indicative of clays and shales. This interpretation implies an inverse relation between gamma counts and grain size.

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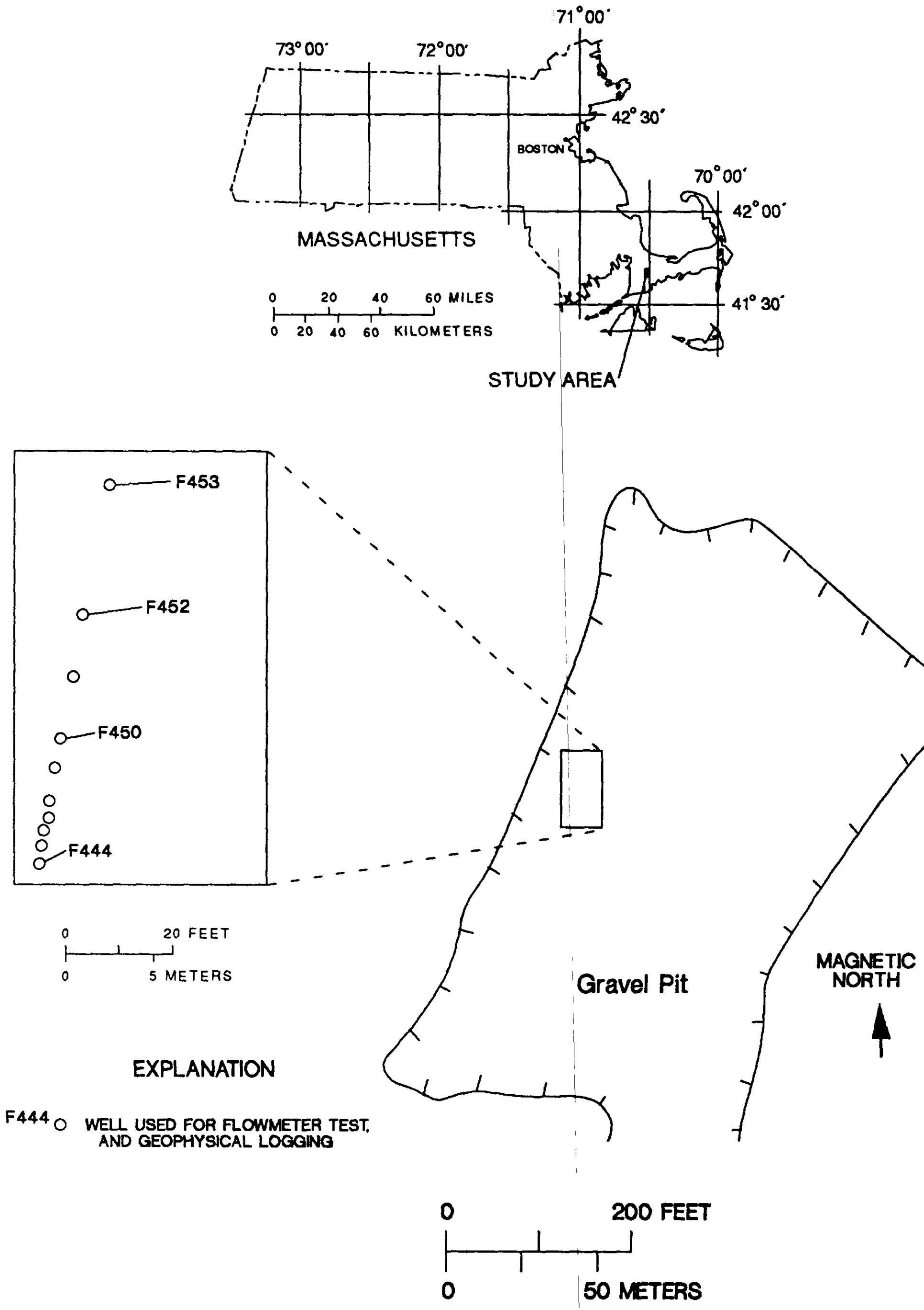
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0 20 40 60 MILES
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41°30'
STUDY AREA
F453
F452
F450
F444
0 20 FEET
0 5 METERS
Gravel Pit
MAGNETIC NORTH
EXPLANATION
F444 ○ WELL USED FOR FLOWMETER TEST, AND GEOPHYSICAL LOGGING
0 200 FEET
0 50 METERS

Figure 1. Location of long-screened wells for flowmeter tests and geophysical logging on Cape Cod, Massachusetts.

The sand and gravel aquifer at the Cape Cod site contains very little fine-grained material; therefore, our investigation was not expected to support this relation. However, it was anticipated that natural-gamma logs might also provide information on grain size for coarser grained deposits, and this hypothesis was a focus of this preliminary investigation.

In the absence of clays in the formation, the neutron-probe response is predominantly affected by hydrogen in the vicinity of the borehole and, consequently, by water content. Accordingly, neutron logs are commonly used to infer porosity in saturated porous media, based on empirical relations which account for the type of saturated medium and the borehole diameter.

DATA ANALYSIS

Typical logs of hydraulic conductivity and gamma and neutron responses are presented in figure 2. Gaps in the hydraulic-conductivity profile correspond to unscreened sections of the casing where threaded joints are located. Hydraulic conductivities from the flowmeter tests span about one order of magnitude. The gamma responses are less than 50 cps, which is typical for a sand and gravel formation, and the neutron responses mostly range from 700 to 900 cps and indicate a high porosity. The two nuclear logs provide a qualitative indication of grain size (gamma log) and a quantitative estimate of porosity (neutron log).

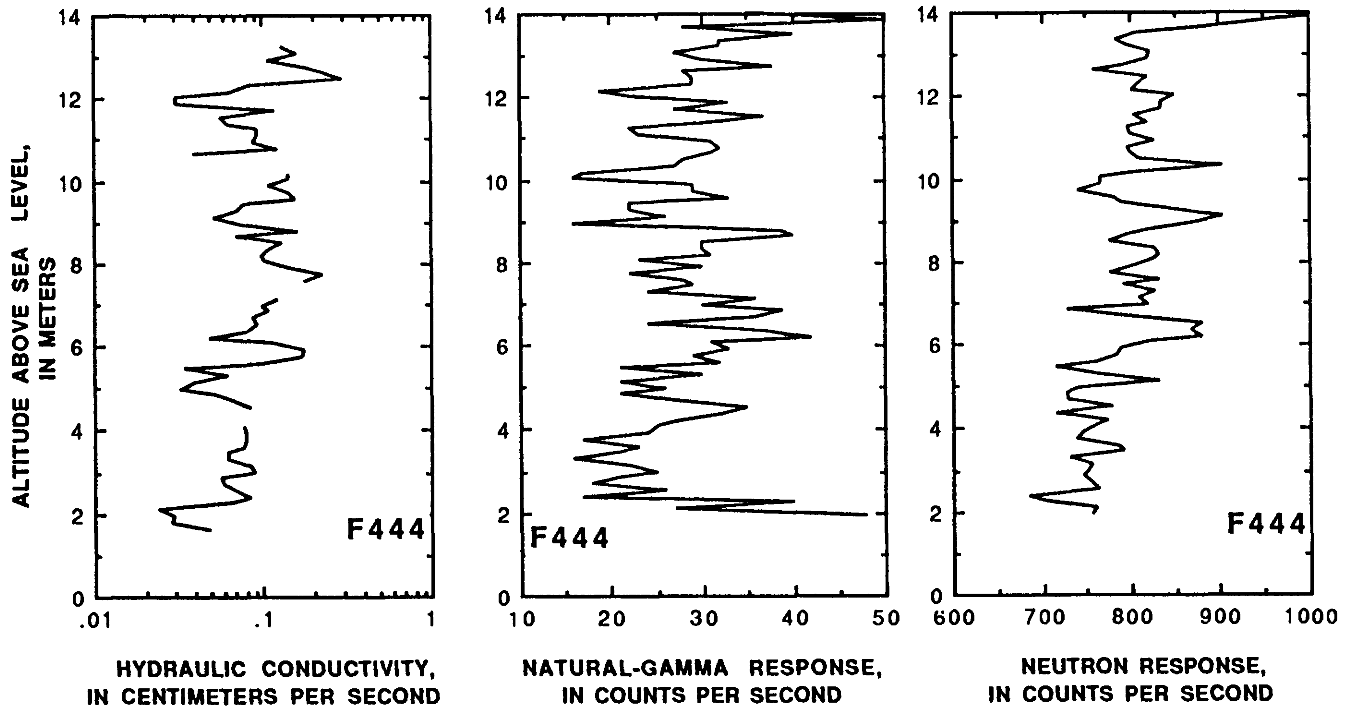

Figure 2. Typical profiles of hydraulic conductivities from flowmeter measurements, and natural-gamma and neutron nuclear logs. Location of well F444 is shown in figure 1.

Numerous efforts have been made to empirically correlate hydraulic conductivity and grain size (Shepherd, 1989). Wolf (1988), using cores obtained from this site, found a close correlation between hydraulic-conductivity values estimated from grain-size distributions (Hazen, 1893; Krumbein and Monk, 1942) and values obtained from permeameter analyses of the cores. Determination of hydraulic conductivity strictly from grain-size measurements, however, does not take advantage of additional information on porosity provided by the neutron log. The Kozeny-Carmen equation (Lamb and Whitman, 1969) was used for this study because it estimates hydraulic conductivity from both porosity and grain size as follows:

$$K = \frac{\alpha}{\nu}\left[\frac{\Phi^3}{(1-\Phi)^2}\right]\frac{d_m^2}{180}, \tag{1}$$

where K is hydraulic conductivity, in centimeters per second, α is specific weight of the fluid, in grams per cubic centimeter, ν is dynamic viscosity of the fluid, in gram-seconds per squared centimeter, d_m is a representative grain size, in centimeters, and ϕ is a dimensionless porosity.

To estimate porosity of the aquifer from the neutron logs, the appropriate calibration constants were determined by identifying the range of neutron counts detected and the range of porosity values expected for the aquifer. A range in porosity of 0.27 to 0.36 was obtained from 69 samples from this site (S. H. Wolf, Mass. Instit. of Tech., written commun., 1989). This range is low compared to the range of effective porosities of 0.33 to 0.41 estimated from small-scale tracer tests conducted near the site (Garabedian and others, 1988). Both methods resulted in similar estimates of the variability in the porosity. Compaction may have caused the porosities measured on the core samples to be lower, and, therefore, the tracer-test porosities of 0.33 to 0.41 were the constraints placed on the transformation used to convert the neutron logs to porosity estimates.

Unfortunately, samples were not collected from these well locations prior to casing installation. Consequently, grain-size data were not available to develop a direct relation between grain size and natural-gamma response. Instead, the hydraulic conductivities from the flowmeter measurements and the porosity estimates from the neutron logs were used in the Kozeny-Carmen equation (eq. 1) to estimate profiles of d_m for three test wells (F444, F450, and F452). An analysis-of-covariance test of the gamma-response data verified that the responses for these three wells originated from the same population, and, therefore, grouping them together was justified. The minimum separation distance between the three wells is 7.2 m, which is at the upper end of the range in horizontal correlation scales (2.9 to 8.0 m) and the minimum vertical separation of 0.15 m is slightly less than the vertical correlation scales (0.18 and 0.19 m) determined for this site from flowmeter and permeameter estimates of hydraulic conductivity (Hess and others, 1991, this Proceedings). Therefore, spatial correlation may exist among the data, but is probably small. For the purpose of this preliminary analysis, the samples were considered independent.

The estimated vertical distributions of grain size were used to define a relation between d_m^2 and the independently acquired natural-gamma logs (fig. 3) for the three wells. A squared value of grain size was used to imply a gamma dependence on surface area. A logarithmic regression analysis resulted in the following relation between d_m^2 and natural-gamma response (NG):

$$d_m^2 = 0.0057(10^{0.05NG}). \tag{2}$$

The coefficient of determination for this regression ($R^2 = 0.415$) indicates that 41.5 percent of the variation in squared grain size can be explained by the variation in gamma response.

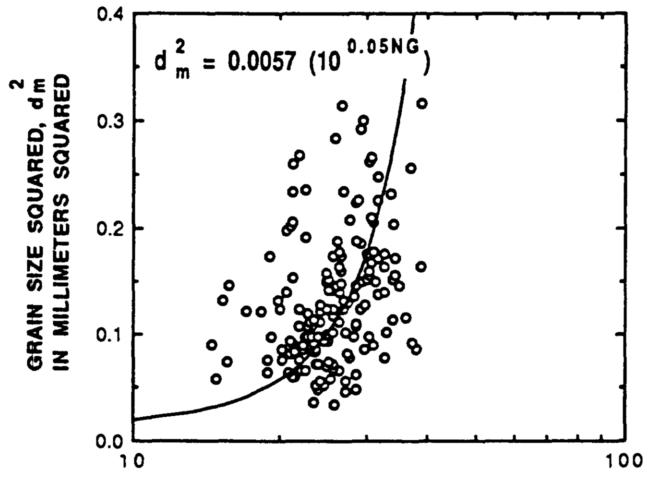

Figure 3. Logarithmic relation of grain size, as determined from the proposed algorithm, to natural-gamma activity for wells F444, F450, and F452. Logarithmic equation is fit by least-squares regression. Locations of wells are shown in figure 1.

The positive slope of the regression equation (fig. 3) indicates a direct relation between gamma response and grain size. This relation is the inverse of that commonly observed and is indicative of a clean sand and gravel deposit in which feldspathic minerals replace clays as the primary source of radioactivity. Barber (1987) performed analyses of grain-size distribution and mineralogy of sediment samples from the vicinity, and reported that quartz and feldspars accounted for approximately 90 percent of the sand- and silt-sized fraction and that only trace amounts (less than 0.1 percent) of clay were present.

The algorithm for predicting hydraulic conductivity from the nuclear logs involved estimating grain sizes from the natural-gamma log using the logarithmic regression equation (eq. 2), computing porosities from the neutron response log using a standard transformation, and substituting these derived parameters into the Kozeny-Carmen equation (eq. 1). To assess the accuracy of this method, the algorithm was applied to the nuclear logs obtained from a well that had not been previously considered (well F453). The resulting distribution of predicted hydraulic conductivity, when compared with the profile obtained from direct flowmeter measurements (fig. 4), indicates that the method developed from nuclear logs does not satisfactorily reproduce the hydraulic conductivity of the aquifer. Errors that contribute to the lack of correlation between estimated and measured values include the inherent statistical uncertainty in the measurement of nuclear counts, which is typically taken to be the square root of the measured counts. Accordingly, the cumulative effect of low gamma counts associated with a lack of clays and low neutron counts associated with relatively high porosities diminishes the predictive capability of the algorithm. The poor correlation ($R^2 = 0.415$) between gamma activity and grain size (eq. 2) also contributed to the lack of agreement between the predicted and measured hydraulic conductivities. Finally, the sampling volumes associated with the nuclear logs and the flowmeter tests are probably different, although each method was assumed to represent specific 0.15-m intervals of the aquifer. A difference in sampling volumes would result in an additional source of error.

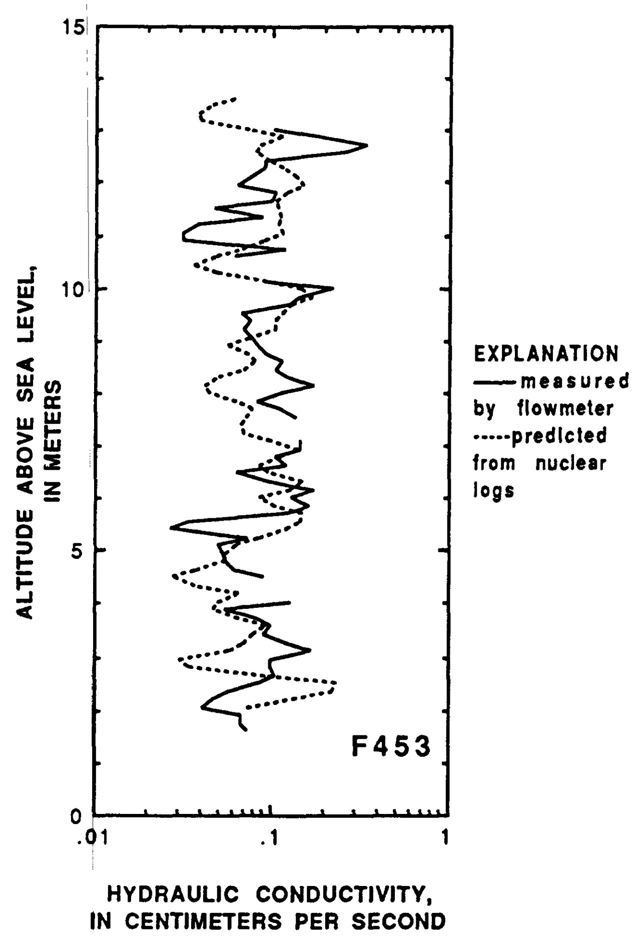

Figure 4. Vertical profiles of hydraulic conductivity, as measured by the flowmeter and as predicted from nuclear logs by the proposed algorithm. Location of well F453 is shown in figure 1.

The statistics of the predicted and measured distributions of hydraulic conductivity, however, agreed well (table 1). The geometric mean hydraulic conductivity predicted for well F453 is 0.08 cm/s (centimeter per second) and is similar to the geometric mean of 0.10 cm/s determined from flowmeter tests in the 10 wells (Hess, 1989). The variances of the natural logarithm of hydraulic conductivity are also similar; the variance of the predicted values for well F453 is 0.21, while the variance of the flowmeter values is 0.26 (table 1).

From a variogram analysis (Journel and Huijbregts, 1978) performed on the predicted hydraulic conductivities, a vertical correlation scale of 0.28 m was computed for well F453. This scale is similar to the vertical correlation scale of 0.26 m determined from flowmeter measurements in all 10 wells (Hess, 1989). The correlation scale was obtained by fitting a negative-exponential model to the calculated variogram by minimizing the sum of squares. This model was of the form

$$\gamma_\chi = \sigma_s^2(1 - e^{-\chi/\lambda}), \tag{3}$$

where γ_χ is the variogram statistic, $\sigma_s{}^2$ is the model sill value (assumed to equal the variance), χ is the separation distance between data pairs compared for the variogram calculation, and λ is the correlation scale. The model fit to the variogram calculated for the hydraulic-conductivity profile predicted for well F453 is shown in figure 5.

Table 1. *Summary of statistical parameters computed from measured and predicted values of hydraulic conductivity (K)*

Well number	Number of measurements	Geometric mean, in centimeters per second	Variance of natural logarithm of K	Vertical correlation scale, in meters
Flowmeter				
All Wells	691	0.10	0.26	0.26
F453	67	.09	.25	.24
Nuclear logs				
F453	73	.08	.21	.28

The variance and correlation scales of the hydraulic-conductivity distribution are needed as input into stochastic transport theories (Gelhar and Axness, 1983; Dagan, 1984) which predict macrodispersivity--the enhanced spreading of solutes in aquifers caused by aquifer heterogeneity--from the statistical properties of the hydraulic-conductivity distribution (see Hess and others, 1991, this Proceedings). The typically cumbersome effort involved in defining the hydraulic-conductivity distribution by other field or laboratory methods, such as flowmeter tests or permeameter analyses of cores, limits the routine use of the stochastic theories in the evaluation of aquifer transport properties. A quick, indirect method of obtaining the needed input parameters, such as the algorithm proposed here, would facilitate this stochastic approach.

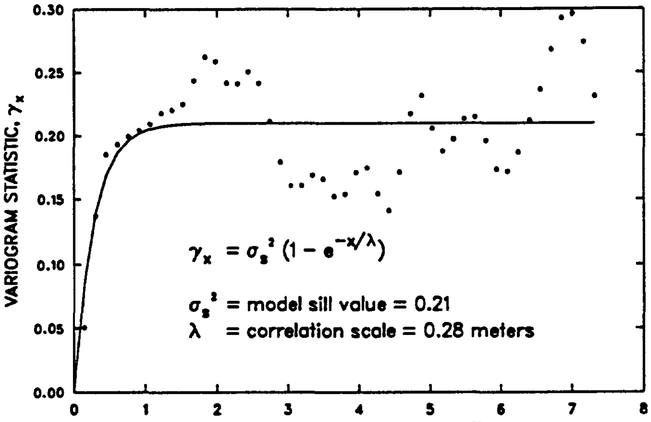

Figure 5. Variogram in the vertical direction of hydraulic conductivities predicted from nuclear logs by the proposed algorithm for well F453. The negative-exponential model was fit to the variogram by minimizing the sum of squares.

SUMMARY AND CONCLUSIONS

Nuclear logs contain information on the stratigraphic variability of the aquifer surrounding a well; the epithermal-neutron log provides a quantitative estimate of porosity and the natural-gamma log provides qualitative information related to grain size. In this preliminary study, hydraulic conductivities were predicted using nuclear logs and an algorithm based on the Kozeny-Carmen equation. Predicted values of hydraulic conductivity generally did not agree well with measures of hydraulic conductivity obtained from flowmeter measurements. The summary statistics of the hydraulic-conductivity distributions, however, including the mean, variance, and vertical correlation scale, were in close agreement for this initial examination of one well. These statistical parameters are needed for stochastic transport theories which predict macrodispersivity based on the variance and correlation scales of the hydraulic-conductivity distribution. Obtaining nuclear logs is a rapid field procedure and, therefore, this approach may be an efficient method for defining appropriate statistical parameters.

Additional work is needed to improve the predictions of hydraulic conductivity by the proposed algorithm. Defining a relation between grain size and natural-gamma activity at a well where grain-size information is available or developing a direct regression relation between hydraulic conductivity and the nuclear logs may improve the estimates.

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CHARACTERIZATION OF A SAND AND GRAVEL AQUIFER USING GROUND-PENETRATING RADAR, CAPE COD, MASSACHUSETTS

By M.D. Knoll,[1,2] F.P. Haeni,[1] *and* R.J. Knight[2]

ABSTRACT

Ground-penetrating radar was used to delineate near-surface geologic conditions in a sand and gravel aquifer on Cape Cod, Massachusetts, in 1990. Radar images yielded information on the overall radar character of the site, including the water table and depositional features in the aquifer to a depth of 40 feet. Some of the radar profiles were used to create a three-dimensional image of the aquifer. Preliminary experiments yielded average electromagnetic propagation velocities for the unsaturated and saturated zones of 0.45 and 0.2 feet per nanosecond respectively. Quantitative analysis of the 1990 radar records is continuing, and the data set is being used to test new computer-processing techniques, which will help visualize the subsurface, and to determine additional properties of the aquifer from the radar data.

INTRODUCTION

Estimation of aquifer properties, such as hydraulic conductivity, porosity, and water saturation, is essential to understanding contaminant transport. Information about the spatial and temporal variability of these properties is difficult to obtain. In some cases, geophysical techniques can provide this information. In particular, there is growing interest in the use of ground-penetrating radar (GPR) to delineate near-surface geologic conditions. Although numerous studies have demonstrated the ability of radar to produce detailed subsurface images, the utility of the technique is limited by the inability to interpret these images in terms of basic material properties. The fundamental premise of this research is that there is a relation between dielectric properties and hydrogeologic properties.

A series of radar experiments was performed at the U.S. Geological Survey Cape Cod Toxic-Substances Hydrology Research site to begin addressing this problem. These experiments constitute the first phase of an integrated research effort, encompassing both laboratory and field work, to determine the physical basis for GPR reflections. This paper summarizes the field work conducted at the site in 1990. This work included (1) determination of the overall radar character of the site; (2) acquisition of a dense, three-dimensional radar data set over a part of the site where the spatial distribution of aquifer properties is well understood; and (3) testing of several new techniques for determining subsurface electromagnetic-propagation velocities.

SITE DESCRIPTION

The radar experiments were conducted in an abandoned gravel pit just south of Otis Air Base on Cape Cod, Mass. (fig. 1). The gravel pit is the location of a multidisciplinary research study involving the transport and fate of contaminants in a shallow, sand and gravel aquifer. Garabedian and LeBlanc (1991, this Proceedings) provide an overview of the research conducted at the site. A particular emphasis of this research has been to determine the effects of aquifer heterogeneity on solute-transport processes. As a result, much is known about the spatial distribution of subsurface physical and chemical properties at the site; this makes the site an excellent one for testing the remote-sensing capabilities of shallow geophysical techniques. The site is particularly well suited for GPR because electrical conductivity and clay content of the aquifer material are low; such conditions cause little intrinsic attenuation and, hence, increase penetration of radar signals in the subsurface.

The site is located on an extensive outwash plain deposited during the retreat of the continental ice sheets from southern New England about 10,000 years ago. The sand and gravel is about 100 ft (feet) thick and is underlain by less permeable silty sand and till (Oldale, 1981). Stratification of the outwash is evident in two shallow trenches and in many of the cores that have been collected at the site (fig. 2). The sand and gravel are in the form of lenses 10 ft or more long and less than 2 ft thick; features such as crossbeds are apparent. The median grain size (by weight) of the outwash is .023 in. (inches), and silt and clay comprise less than 1 percent of the deposit (LeBlanc, 1984; Wolf, 1988). The sediment grains are composed predominantly of quartz and feldspar, and have a surface coating of iron oxide and, in some zones, manganese oxide.

Regional ground water is unconfined and moves southward at a rate of about 1.4 ft/d (feet per day) (LeBlanc and others, 1991). The estimated average horizontal hydraulic conductivity of the aquifer is 280 to 380 ft/d, and the effective porosity is 39 percent. These characteristics were determined from aquifer, borehole flowmeter, and tracer tests conducted in or near the gravel pit (Garabedian and others, 1988; Hess, 1989; LeBlanc and others, 1991). The water table at the site is nearly horizontal but ranges in depth from 10 to 20 ft because of variations in land-surface elevation. The height of the capillary fringe is small (3 to 6 in.), because of the coarse texture of the sediments.

RADAR METHODOLOGY

Collection of Radar Data

A commercial radar system (SIR System-8) manufactured by Geophysical Survey Systems, Inc. (GSSI)[3] was used. This system consists of a transmitter, receiver, control unit, digital tape recorder, and graphic output device.

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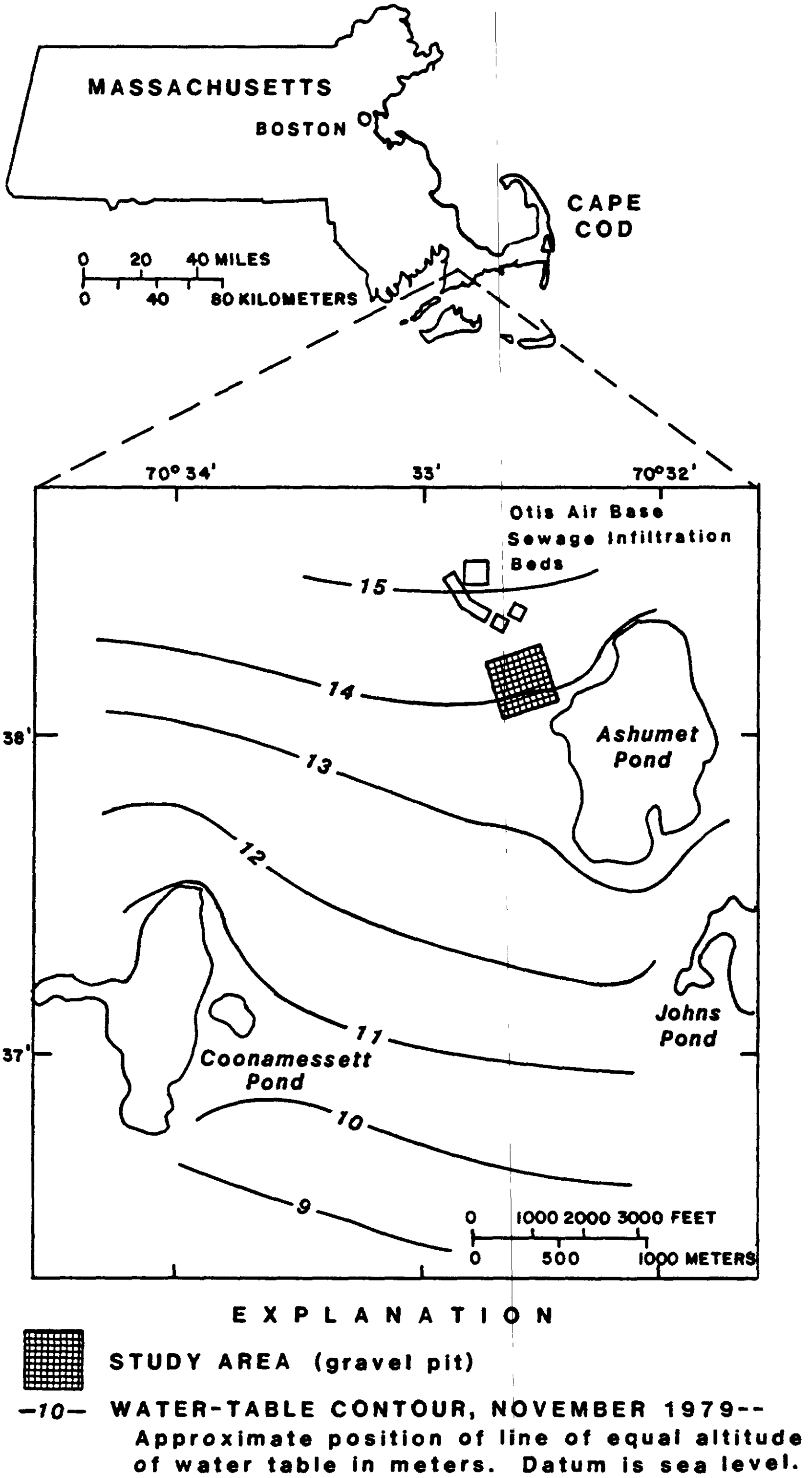
[3] The use of brand, firm, or trade names in this paper is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

The transmitter produces a high-voltage pulse that is applied to an antenna, which radiates the energy into the ground. The process of transmitting and receiving radio-frequency pulses of electromagnetic energy is repeated as the antennas are pulled across the ground. The high repetition rate produces a virtually continuous cross-sectional image of variations in subsurface dielectric properties. The high repetition rate of the radar, together with the slow speed of travel of the antennas over the ground, produced a radar record that contained approximately 12 radar scans per foot of antenna travel.


MASSACHUSETTS
BOSTON
CAPE COD
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15
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Ashumet Pond
Johns Pond
Coonamessett Pond
0 1000 2000 3000 FEET
0 500 1000 METERS
EXPLANATION
STUDY AREA (gravel pit)
—10— WATER-TABLE CONTOUR, NOVEMBER 1979--
Approximate position of line of equal altitude of water table in meters. Datum is sea level.

Figure 1. Location of study area, Cape Cod, Massachusetts. (From Hess, 1989.)

Signal Processing of Radar Data

The raw radar record contains numerous artifacts and distortions that need to be corrected or accounted for prior to quantitative interpretation. Digital recording and postacquisition processing were necessary for the three-dimensional and propagation velocity experiments. A commercial software package (RADAN) that runs on a personal computer was used to complete most of the processing. Synthetic data sets were generated to test the action of the commercial routines. Additional software was developed to experiment with different ways of displaying the data.

The following processing sequence was used:

(1) The data were downloaded from field tapes to the computer.

(2) Variations in antenna movement speed were corrected by rubber-sheeting.

(3) Adjacent scans were averaged, or stacked, so that the total number of scans was reduced. This process also serves to improve the signal-to-noise ratio. In the three-dimensional survey, four scans were stacked to form one scan; the final data density was then three scans per foot.

(4) The data were processed to recover amplitude information.

(5) The data were filtered through various frequency bands to determine which frequencies contain real reflections and which are purely noise.

(6) A mixing process was applied to the data, which is equivalent to taking a weighted running average. This tends to increase continuity of reflectors provided they are not steeply dipping.

Display of Radar Data

The final step in the processing sequence is data display. Many display techniques may be used, including wiggle-trace, wiggle-trace with variable area fill, and variable-density plots. In addition, data can be plotted with normal or reverse polarity, at various amplitude levels, and with various colors or shades of gray.

The RADAN software has limited display capabilities. Three programs were developed to improve display of the Cape Cod radar data. The first program (DISPLA) overlays wiggle traces on two-dimensional color line scan plots and also accurately converts screen colors to hardcopy colors. The second program (STVIEW) was designed for interactive two-dimensional interpretation. The user is able to bring up data in windows, zoom in on the specific reflections, and determine the amplitude and position of individual samples using a mouse. The program supports wiggle traces, line scans, and color and gray scale for two-dimensional data. Best-fit lines and hyperbolas can be overlain on the data to aid in velocity analysis. Finally, STVIEW can be used to produce high-resolution wiggle trace plots using a laser printer. The third program (DATAVIEW) is an interactive three-dimensional interpretation program developed on a Unix-based workstation. The data are displayed in a cube that may be sliced, peeled away, rotated, or magnified. Although this research is in its infancy, many benefits are expected from the ability to display radar data in these new ways.

RESULTS TO DATE

Reconnaissance Mapping

A series of profiles was run to determine the overall radar character at the site. The profiles were obtained using dual 80 MHz (megahertz) antennas--one as a transmitter and one as a receiver. Recording time was set at 900 nanoseconds. The antennas were towed along roads and across open space at the site. The locations of anomalous features were noted on the radar record and additional work with a 300 MHz antenna was done to explore these anomalies further.

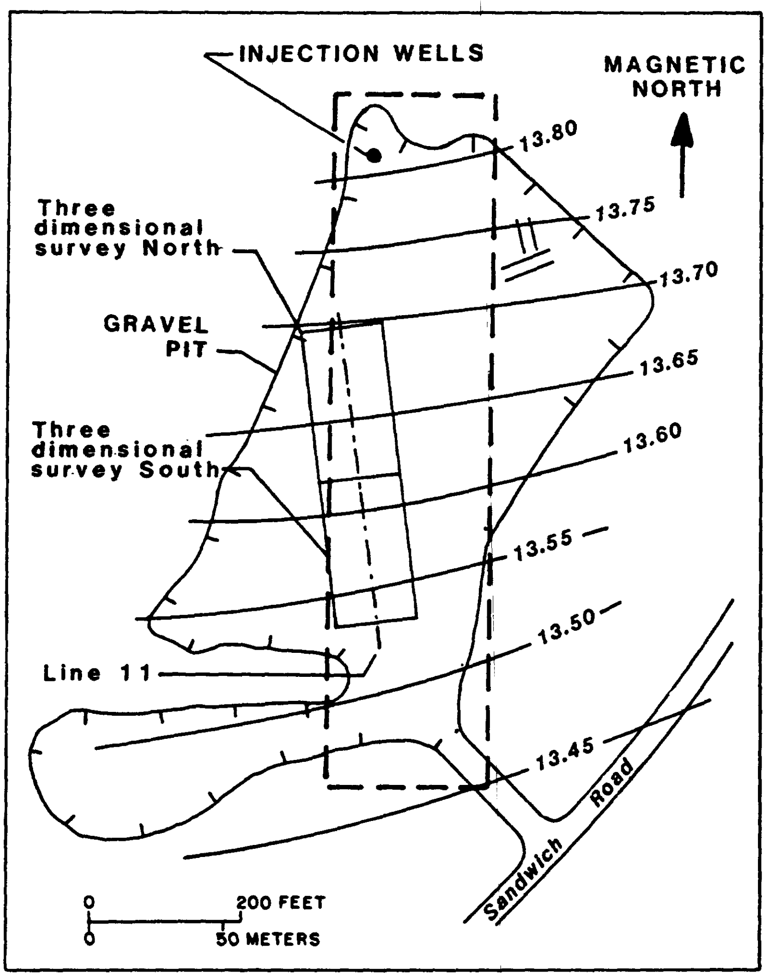
The most obvious feature in the records is a strong, continuous subhorizontal reflection, which was traced throughout the area and is interpreted as the water table. The records also showed sequences of short reflectors. In the northern part of the site, these reflectors are subhorizontal; in the southern part of the site, they dip to the south and form part of a large synclinal feature. South of the site, the beds dip toward Ashumet Pond. These dipping beds are interpreted as a collapse structure associated with the Ashumet Pond kettle hole. The edge of this structure is apparent in the three-dimensional data described below.

Three-Dimensional Survey

The three-dimensional survey was located in the open part of the gravel pit just west of the multilevel sampler array shown in figure 2. This location was chosen for several reasons. It included the area where research is ongoing to characterize small-scale variations in hydraulic conductivity (Wolf, 1988; Hess, 1989; Hess and others 1991, this Proceedings). Also, the area extends part way into the multilevel sampler array, which allows comparison of aquifer properties determined from radar data with estimates derived from the large-scale tracer test. Finally, the area includes part of the synclinal feature described above.

The three-dimensional survey, which was divided into a northern and southern area (fig. 2), consisted of 20 lines run south to north, and 16 lines run east to west. The north-south lines are spaced 4.5 ft apart, except in the east where the multilevel samplers disrupted the pattern. The east-west lines were spaced 54 ft apart, except in the area where detailed hydraulic conductivity studies have been conducted; there, the lines were spaced 9 ft apart where possible. Data acquisition was completed in one 8-hour day.

Each line of the three-dimensional data was processed separately as previously described. An example of the final result for one of the lines (line 11) is shown in figure 3. These data were plotted using the program DISPLA. The water table, which is flat, is clearly evident about a third of the way down the record. There is also a break in the slope of the reflections that cross the water table in the southern area. This break in slope can be used to determine the velocity contrast across the water table. The subhorizontal reflectors in the northern area and the southward dipping reflectors in the southern area are also evident. The interpreted depth of penetration of the radar signal is approximately 40 ft.



EXPLANATION

⌐┘ AREA OF MULTILEVEL SAMPLER ARRAY

☐ AREA OF RADAR SURVEY

═ TRENCHES

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

—·—· SINGLE RADAR LINE

Figure 2. Location of radar experiment in relation to other experiments conducted at the research site. Location of gravel pit shown in figure 1.

A three-dimensional display of the southern part of the area is shown in figure 4. The water table is visible as a subhorizontal surface and the dipping reflectors can be identified.

Velocity Experiments

A series of experiments was conducted to determine subsurface electromagnetic propagation velocities at the site. The propagation velocity in the unsaturated zone was determined by dividing the depth to the water table, as determined by direct measurements in wells, by half the two-way traveltime. Propagation velocities determined by this method ranged from 0.44 to 0.51 ft/ns (feet per nanosecond). A velocity of 0.45 ft/ns was used in data processing to correct for land-surface elevation changes. This velocity corresponds to a dielectric constant of about 4.5. Using a simple mixing law (the complex refractive index method of Warton and others (1980)), this average dielectric constant can be used to estimate porosity. A preliminary analysis gives porosity values of 32 to 48 percent, depending on the amount of surface-bound water in the pore space.

The propagation velocity in the saturated zone was determined from common-midpoint gathers to be approximately 0.2 ft/ns. This correlates well with the range of saturated velocities determined from time-domain reflectometry experiments conducted by other researchers at the site (David Rudolf, University of Waterloo, written commun., 1990).

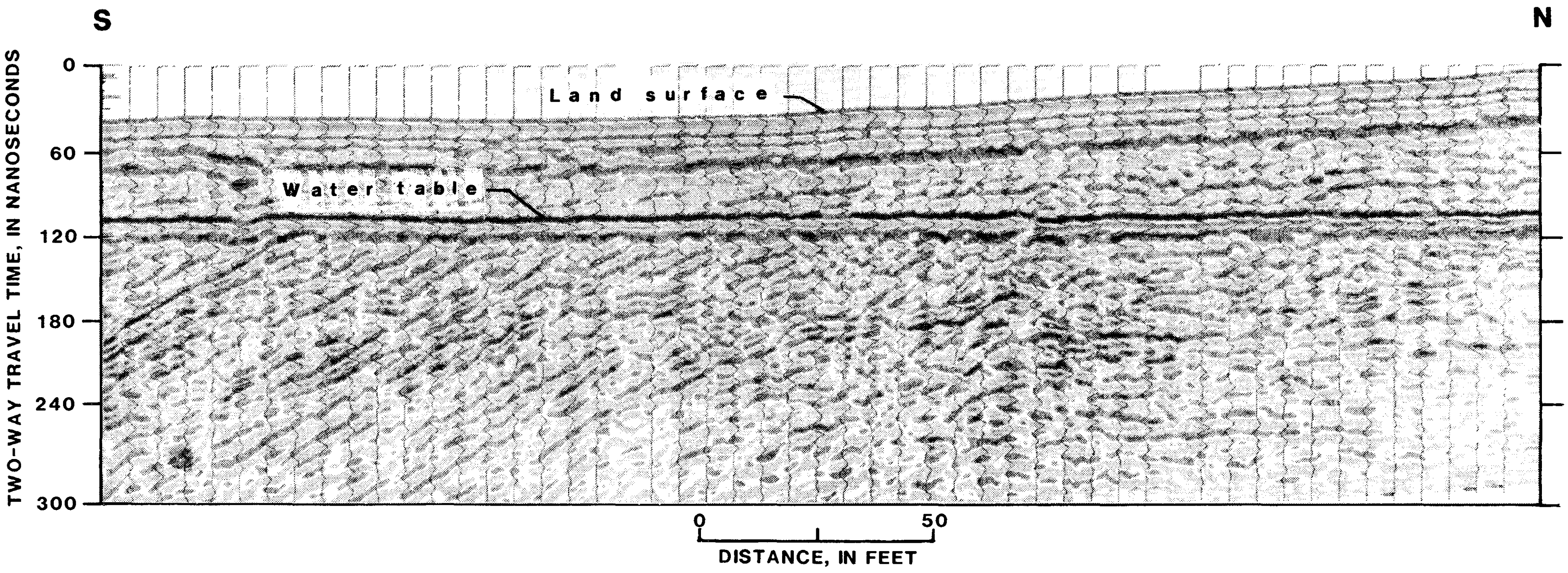


Figure 3. Processed radar image for line 11. Radar scans plotted every 4 inches along profile; wiggle traces plotted every 6.15 feet. Total two-way traveltime is 306 nanoseconds. Estimated depth of penetration is 40 feet.

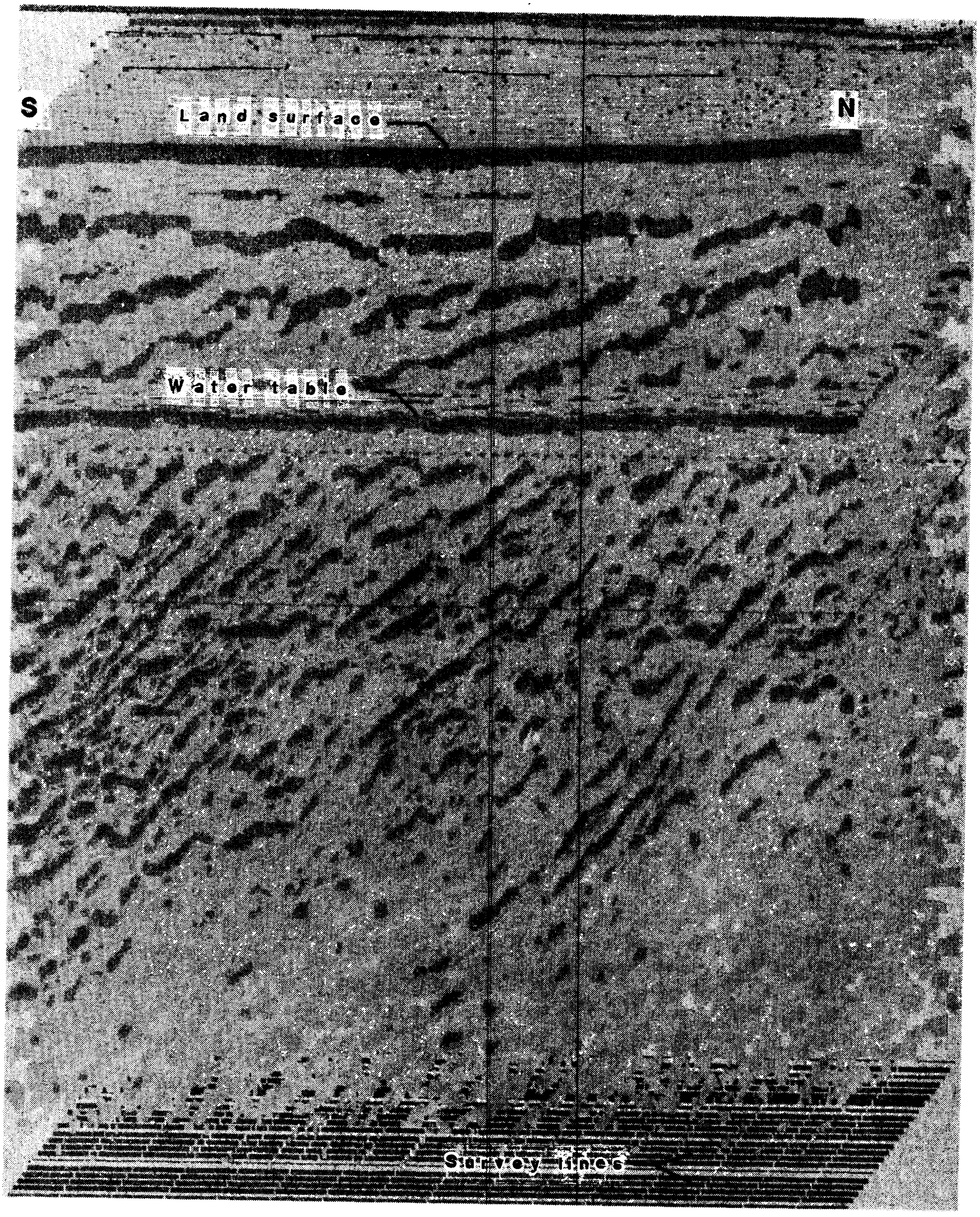

S
N
Land surface
Water table
Survey lines
300

Figure 4. Three-dimensional radar image over southern part of study area (south of line T). Horizontal distance is 170 feet; vert distance is 40 feet.

CONCLUSIONS

The 1990 field work showed that ground-penetrating radar could define the position of the water table and depositional features in a sand and gravel aquifer at the Cape Cod Toxic-Substances Hydrology Research site. Synclinal depositional features and the water table could be identified on the raw field records, and computer processing enhanced the interpretation. Three-dimensional images of the subsurface were produced. Preliminary experiments yielded average electromagnetic propagation velocities for the unsaturated and saturated zones of 0.45 and 0.2 ft/ns, respectively. Quantitative interpretation of the radar data and how the data relate to the hydrogeologic properties of the aquifer is continuing.

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CHARACTERIZATION OF LARGE-SCALE AQUIFER HETEROGENEITY IN GLACIAL OUTWASH BY ANALYSIS OF SLUG TESTS WITH OSCILLATORY RESPONSES, CAPE COD, MASSACHUSETTS

By Roland K. Springer[1] *and* Lynn W. Gelhar[1]

ABSTRACT

An extensive slug-testing program was carried out to characterize the large-scale spatial variability of horizontal hydraulic conductivity in glacial outwash on Cape Cod, Massachusetts. A secondary objective of the program was to determine the usefulness of slug tests for measuring hydraulic conductivity in very permeable sediments. A total of 338 observation wells were tested in a 17-square-mile area. Of these, 105 wells exhibited an oscillatory response to an instantaneous displacement of the water level. In order to be able to analyze all the slug tests, the method of Bouwer and Rice, presented in 1976 in volume 12 of the journal, Water Resources Research, was modified to include inertial effects in the wells. This modification, which provides a treatment for oscillatory responses, yields hydraulic-conductivity values for the nonoscillatory case that are about 10 percent lower than values obtained by the method of Bouwer and Rice. Preliminary analysis shows large variation in hydraulic-conductivity values, which range from 0.26 to 1,570 feet per day and have a geometric mean of 141 feet per day. The standard deviation of the natural logarithm of the hydraulic conductivity is 1.4. Results indicate a zone of low conductivity, less than 20 feet per day, located greater than 100 feet below the water table. Hydraulic conductivity increases upwards, with zones of conductivity greater than 500 feet per day commonly located 25 to 60 feet below the water table.

INTRODUCTION

A number of studies have been performed at the U.S. Geological Survey's Cape Cod Toxic-Substances Hydrology Research site to determine the range and spatial scales of aquifer heterogeneity. The purpose of this study is to describe the variability of horizontal hydraulic conductivity at an even larger scale using slug tests, a simple, cost-effective method for obtaining point values of conductivity. This paper presents interim results of this ongoing research.

Many methods for analyzing slug tests have been proposed (Cooper and others, 1967; Van Der Camp, 1976; Kipp, 1985). The one applied here is that of Bouwer and Rice (1976), in which varying diameters, lengths, and positions of well screens in the unconfined aquifer are taken into account. In their analysis, an electrical-resistance-network model was used to parameterize the radius over which drawdown is dissipated around a well following an instantaneous displacement of the water level.

One effect which is not described by Bouwer and Rice (1976) is that of oscillatory responses to an initial displacement. This can occur in highly permeable aquifers, in which the inertia of the recovering water column is great enough to cause oscillations. A third of the wells tested in this study exhibited various degrees of oscillation in their response to an instantaneous displacement.

Kipp (1985) presents an analysis in which a momentum balance relates the hydraulic head at the top of the water column to the head at the bottom of the column. When a similar analysis is incorporated into the method of Bouwer and Rice (1976), the resulting governing equation resembles the damped spring-mass equation, which has both oscillatory and nonoscillatory modes. This modified method, which was applied to all the wells tested at the Cape Cod site, provides meaningful results for both types of response.

Values of horizontal hydraulic conductivity were obtained using this new method of analysis for 338 wells slug-tested in a 17-square-mile area of Cape Cod, Mass. These values ranged from less than 1 to greater than 1,000 ft/d (feet per day). Results indicate a low-permeability zone, also reported by LeBlanc (1984a), at the bottom of the aquifer.

SITE DESCRIPTION

The area that includes the observation wells is approximately 3.5 mi (miles) wide and 5 mi long (fig. 1) and is part of the glacial outwash plain that forms most of western Cape Cod. The large-scale tracer test described by LeBlanc and others (1991) was conducted in an abandoned gravel pit located at the northern end of the area. The sediments at the site (LeBlanc, 1984b) consist of stratified sand and gravel, which overlies fine sand, silt, and dense sandy till. Bedrock lies nearly 250 ft (feet) below the ground surface.

The network of 338 observation wells is arranged into 139 clusters, with each cluster having from one to eight wells screened at various depths. The range in well depths is from the water table to 200 ft below the water table. Most of the well screens are 2 ft long and are made of 0.010-in.(inch)-slot, 2-in.-diameter, polyvinyl-chloride pipe. However, several wells have screens up to 20 ft long. Almost all of the observation wells were installed with a hollow-stem auger.

SLUG-TEST FIELD PROCEDURE

The slug tests were conducted by first lowering a capped steel pipe 4 ft below the ambient water level and then allowing the water level to reequilibrate. Next, the pipe was quickly pulled out of the water to create an instantaneous drop of the water level inside the well. The recovery was

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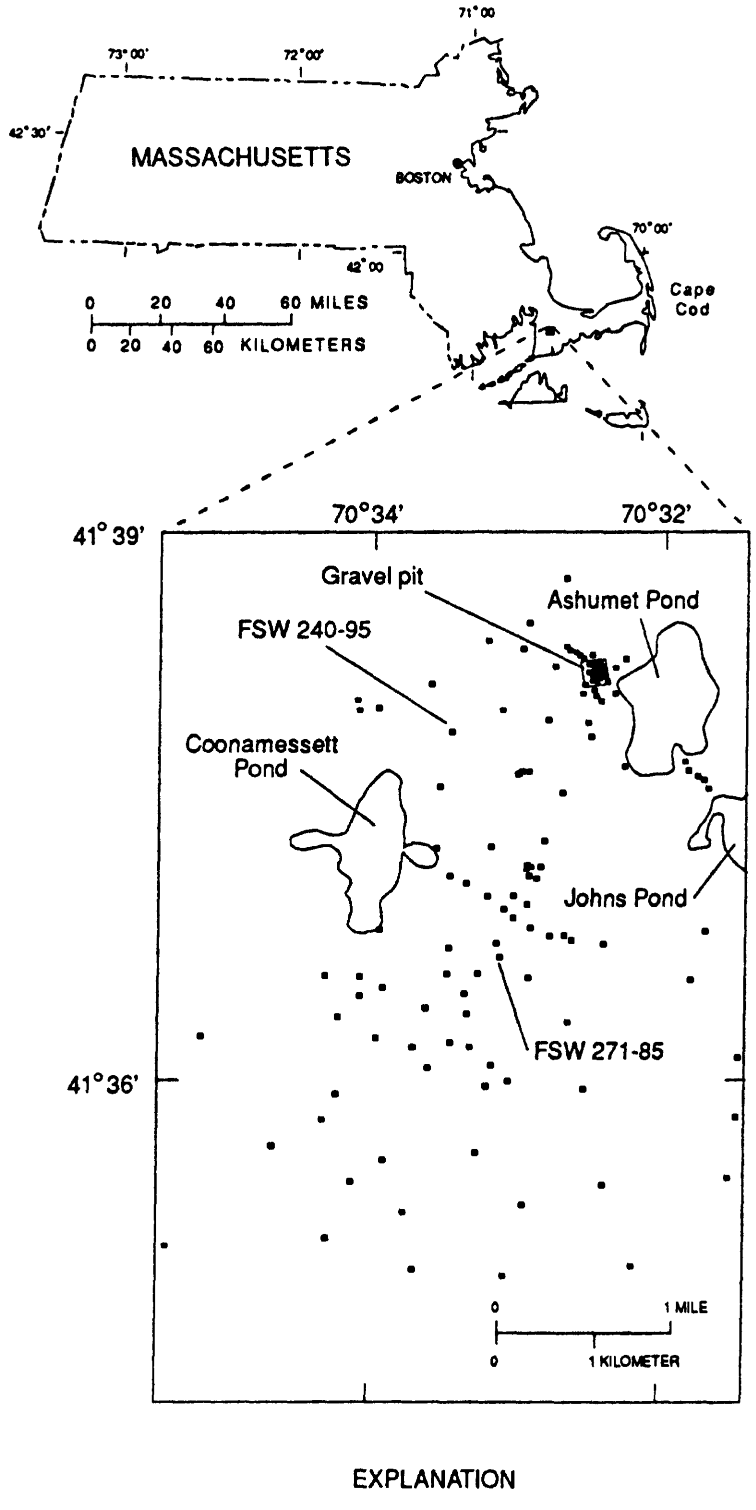
71°00
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MASSACHUSETTS
BOSTON
70°00'
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0 20 40 60 KILOMETERS
70°34'
70°32'
41°39'
41°36'
Gravel pit
Ashumet Pond
FSW 240-95
Coonamessett Pond
Johns Pond
FSW 271-85
0 1 MILE
0 1 KILOMETER
EXPLANATION
• OBSERVATION WELL

Figure 1. Locations of observation wells in which slug tests were conducted.

monitored by measuring the water level at 0.2-second intervals. Because of the short recovery time for most of the wells (usually less than 20 seconds), a pressure transducer and data logger were used to measure the water level as a function of time. The transducer was placed 7 ft below the static water level. Representative responses are shown in figure 2a (nonoscillatory, with the drawdown plotted on a logarithmic scale) and figure 2b (oscillatory).

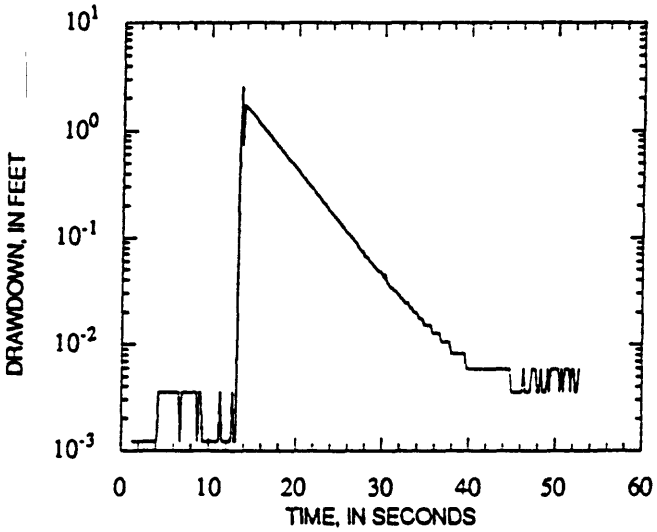

Figure 2a. Nonoscillatory response at well FSW 240-95.

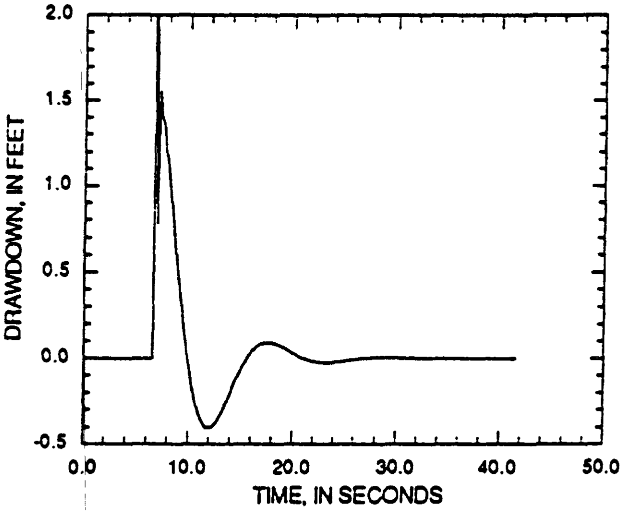

Figure 2b. Oscillatory response at well FSW 271-85.

SLUG-TEST ANALYSIS

The method of Bouwer and Rice (1976; Bouwer, 1989) is based on the Thiem equation for the steady-state flow into a well when the water level in the well is below the water level in the aquifer. The flow is calculated as

$$Q = 2\pi KD\,(h_o-h_s)\frac{1}{ln(R_e/r_w)}, \qquad (1)$$

where Q = volume rate of flow into the well, K = hydraulic conductivity of the aquifer near the well, D = length of perforated screen, and (h_o-h_s) = difference in head between the aquifer and the well screen, assumed here to equal the drawdown, w, of the water level in the well. The variable r_w is the radial distance from the center of the well to the "undisturbed" aquifer, the location at which the hydraulic conductivity equals the preinstallation conductivity. For this site, r_w was assumed to be equal to the outside radius of the well screen. The variable R_e, the radius over which the drawdown is propagated, takes into account the effect of vertical flow around the well screen. R_e was parameterized by Bouwer and Rice (1976) using an electrical-resistance-network model that assumed isotropic hydraulic conductivity. These variables are shown in figure 3.

The governing equation for the system is the continuity equation inside the well,

$$\frac{dw}{dt} = -\frac{Q}{\pi r_c^2}, \qquad (2)$$

where r_c is the inside radius of the well pipe and w is the drawdown of the water level in the well. By combining equation 1 with equation 2, which assumes constant hydraulic head within the well pipe, the following expression for hydraulic conductivity (K) is obtained:

$$K = \frac{r_c^2}{2D}\, ln(R_e/r_w)\, b, \qquad (3)$$

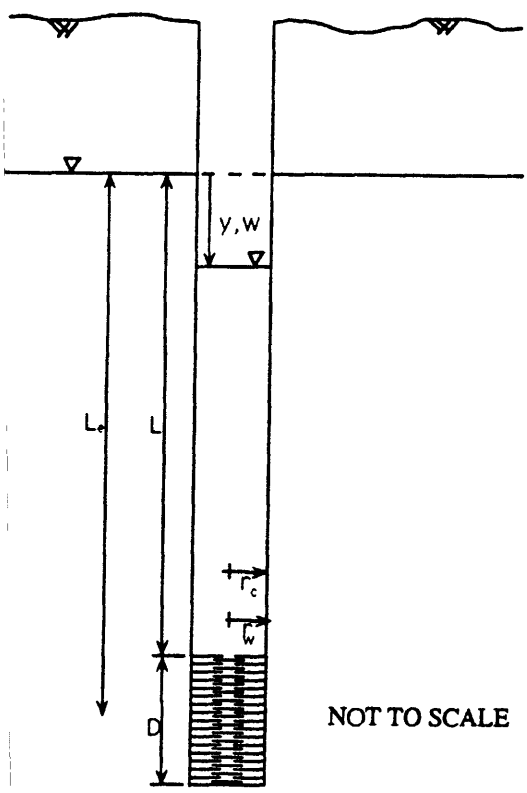

Figure 3. Schematic diagram of observation well.

where b is the slope of the water-level recovery curve, with the abscissa being time and the ordinate being the natural logarithm of drawdown.

MODIFICATION OF THE ANALYSIS TO ACCOUNT FOR INERTIAL EFFECTS

The above analysis works for wells in which the recovery of the water level plots linearly on a semilogarithmic scale, which is the case for wells in zones of low to medium hydraulic conductivity. However, for wells in zones of higher conductivity (greater than about 200 ft/d), the extremely fast recovery often results in an inertial effect which causes oscillations that must be accounted for in the analysis. This is because, in an accelerating water column, pressure is not hydrostatic and the head in the well screen does not equal that at the top of the water column. Thus, a relation between drawdown at the well screen (h_o-h_s) and drawdown at the surface of the water column (w) is required. By applying a momentum balance to the system, we obtain the relation

$$\frac{d^2w}{dt^2} + \frac{g}{L_e}w = \frac{g}{L_e}(h_o-h_s) \ , \qquad (4)$$

where g = gravitational acceleration and L_e = effective well length (L+D/2 in fig. 3).

Using equations 1 and 2 to obtain the (h_o-h_s) term in equation 4, we can obtain a response equation for the drawdown, w, which accounts for inertial effects. The equation can be written in dimensionless form, which facilitates type-curve matching, as

$$\frac{d^2w^*}{d\underline{t}^2} + F\frac{dw^*}{d\underline{t}} + w^* = 0 \ , \qquad (5)$$

where

$$\underline{t} = \sqrt{g/L_e}\, t, \qquad (5a)$$

$$F = \sqrt{g/L_e}\,\frac{r_c^2}{2KD}\ln(R_e/r_w)\text{, and} \qquad (5b)$$

$$w^* = w/w_o \ . \qquad (5c)$$

The variable $\underline{t}$ is dimensionless time, F is the "well factor," w* is dimensionless drawdown, and w_o is the initial drawdown.

Equation 5 is the classical equation for a damped spring. It has three solutions: (1) underdamped (oscillatory), in which F < 2; (2) critically damped, in which F = 2; and (3) overdamped (nonoscillatory), in which F > 2. Figure 4a shows the solutions for various values of F.

By squaring the values of w* for the underdamped curves and plotting them on a semilogarithmic plot (fig. 4b), type curves are obtained which can then be used to match plots of squared drawdown as a function of dimensionless time from slug tests. For the overdamped responses, squaring is not necessary in order to plot the recovery on a logarithmic scale. From the type-curve match, the well factor F can be obtained, from which the hydraulic conductivity can be calculated by equation 5b. As an example, the response of well FSW 271-85 (fig. 2b) is plotted as a function of dimensionless time in figure 5. The corresponding type-curve match is F = 0.34, which yields a hydraulic conductivity of 317 ft/d.

The inertial analysis yields results for both the oscillatory and nonoscillatory responses encountered at the Cape Cod site. Because inertia also has an effect in wells exhibiting a nonoscillatory response, neglecting inertia results in an overestimation of the hydraulic conductivity. The correction obtained by the analysis presented here decreases values obtained from the Bouwer and Rice (1976) method by about 10 percent.

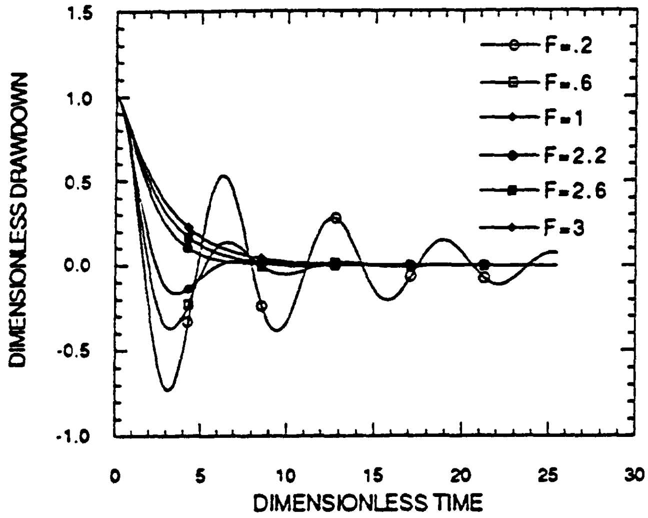

Figure 4a. Slug-test type curves.

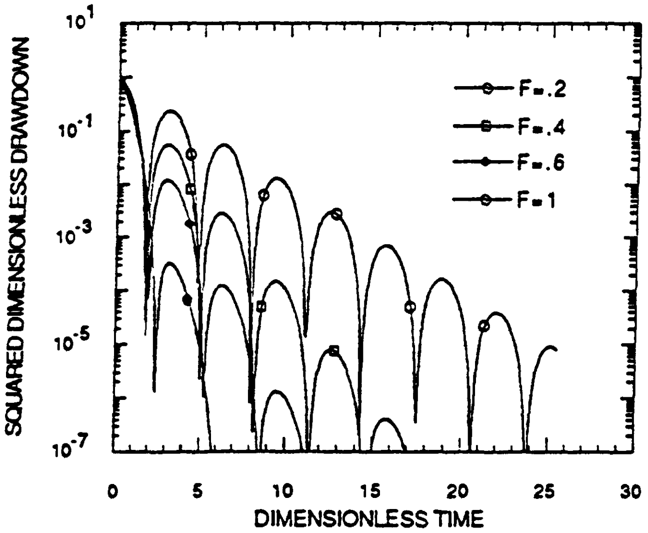

Figure 4b. Slug-test type curves used for oscillatory-response matching.

PRELIMINARY RESULTS OF SLUG TESTS

Analysis of the water-level recovery curves provides a general description of the heterogeneity of the aquifer at the Cape Cod site. The hydraulic conductivity ranges over four orders of magnitude, with values of 0.26 to 1,570 ft/d, and arithmetic and geometric means of 260 and 141 ft/d, respectively. The standard deviation of the natural logarithm of the hydraulic conductivity is 1.4. The average conductivity is in the range of values reported by LeBlanc (1984a), Garabedian and others (1988), Hess (1989), and LeBlanc and others (1991).

The wells deeper than 100 ft below the water table delineate a low-permeability zone (less than 20 ft/d) that is consistent with the low values of hydraulic conductivity reported by LeBlanc (1984a) for the finer grained sediments beneath the sand and gravel. Many wells screened near the water table yield a medium value of hydraulic conductivity (100-300 ft/d), and the wells with highest conductivity (greater than 500 ft/d) are often screened at depths of 25 to 60 ft below the water table. The large range of hydraulic-conductivity values obtained, from less than 1 to greater than

1,000 ft/d, suggests that the slug test is sensing significant effects of actual variations in the aquifer and is not greatly affected by effects related to well installation.

Although the large-scale vertical trends noted above are suggested by the entire data set, the conductivity also varies greatly on smaller scales. Because of this great variability, these general large-scale trends would be very difficult to detect with only a few wells or wells closely spaced in a small area.

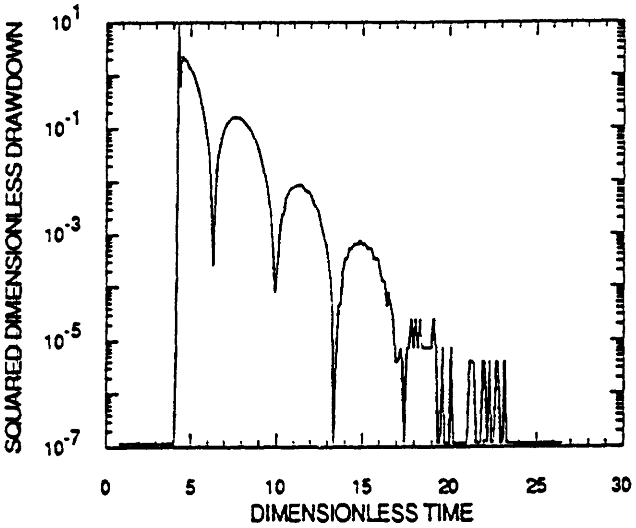

Figure 5. Oscillatory response at well FSW 271-85 for type-curve matching.

CONCLUSION

A method for analyzing oscillatory responses of slug tests in unconfined aquifers that have a high horizontal hydraulic conductivity has been developed. This analysis accounts for oscillatory and nonoscillatory responses and provides a small downward correction to hydraulic-conductivity values obtained from the Bouwer and Rice analysis for the latter. Water levels in approximately one-third of the observation wells at the Cape Cod site oscillate in response to a slug test. Thus, the new method will be applicable to sand and gravel aquifers exhibiting high hydraulic conductivity similar to that on Cape Cod.

Results from a large-scale slug-testing effort have shown the presence of a zone of low hydraulic conductivity (less than 20 ft/d) located more than 100 ft below the water table. At medium depths (25 to 60 ft below the water table), hydraulic conductivity often exceeds 500 ft/d. The geometric mean for all the wells is 141 ft/d--a value similar to that calculated in other studies. Because they are inexpensive and easy to conduct, slug tests are a practical tool for characterizing large-scale heterogeneity in aquifers.

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DESIGN AND OPERATION OF AN INFILTRATION EXPERIMENT IN UNSATURATED GLACIAL OUTWASH, CAPE COD, MASSACHUSETTS

By Denis R. LeBlanc[1], David L. Rudolph[2], R. Gary Kachanoski[2,3], *and* Michael A. Celia[4]

ABSTRACT

Flow and solute transport through the unsaturated zone were observed in detail during an infiltration experiment conducted in a sand and gravel glacial outwash on Cape Cod, Massachusetts. The objectives of the experiment were to test new field methods to measure flow and solute transport in the unsaturated zone and to improve understanding of unsaturated-zone hydrology in heterogeneous sediments. Soil-moisture content, pressure, and solute concentration were measured during a series of infiltration experiments conducted on a test plot 2 meters wide and 10 meters long. Instrumentation was installed to a depth of 2 meters and included 168 pairs of time-domain reflectrometry probes and 112 suction-lysimeter/tensiometers. The 20- square-meter plot was irrigated through sprinkler nozzles set 1.5 meters above ground surface. The experiments were divided into two sets. The first set focused on transport of solutes under steady-flow conditions with irrigation rates ranging from 7.9 to 37.0 centimeters per hour. The second set focused on transient water flow during several wetting and drying cycles. Analysis of the data will focus on spatial variability of the response of the unsaturated zone to irrigation and the ability of numerical models to simulate the experimental results.

INTRODUCTION

The movement of water and chemicals in the unsaturated zone is a critical component of ground-water contamination problems. Many contamination problems begin with transport of chemicals through the unsaturated zone to the water table. Examples include contamination by agricultural chemicals, sewage disposal, and fuel spills. Despite the importance of the unsaturated zone as a source to the saturated zone, few field studies have examined the movement of water and chemicals through the region between the soil zone and the water table.

The processes of flow and solute transport in the unsaturated zone are very complex, in large part because hydraulic properties such as hydraulic conductivity vary greatly as a function of water content and, consequently, the flow regime is highly nonlinear. The heterogeneity of deposits such as glacial outwash adds to the complexity.

A combination of field and modeling studies may be the best approach for developing an understanding of flow and solute-transport processes in the unsaturated zone. Few studies that combine field experiments and modeling have been made of these processes (examples include Wierenga and others, 1988, and Jury and others, 1990) because unsaturated-zone processes are complex, field measurements and collection of water samples are difficult, and numerical modeling is computationally challenging. An infiltration experiment was conducted in the unsaturated zone at the Cape Cod Toxic-Substances Hydrology Research Site (fig. 1) in July 1990 to address these issues. The experiment was conducted in a sand and gravel glacial outwash and included detailed measurements to describe flow and solute transport during irrigation of a densely instrumented test area. This paper describes the objectives, design, and operation of the experiment.

This work was a joint effort by the University of Waterloo and the University of Guelph in Ontario, Canada; Princeton University in Princeton, N.J.; and the Toxic-Substances Hydrology Program of the U.S. Geological Survey.

OBJECTIVES OF THE EXPERIMENT

The infiltration experiment was designed to obtain a detailed data set on water flow and solute transport in the unsaturated zone at a field site that can be used to (1) compare methods for measuring unsaturated-zone hydraulic and transport properties; (2) describe the spatial variability of these properties; and (3) test methods, particularly numerical simulation, for analyzing flow and solute transport in the unsaturated zone. More specifically, the data will also be used to (1) evaluate the use of time-domain reflectrometry (Topp and others, 1980) for measurement of soil-moisture content and solute-mass flux, (2) determine the relation between average unsaturated hydraulic conductivity and average soil-moisture content at the field scale, (3) estimate longitudinal dispersivity as a function of travel distance and soil-moisture content, and (4) investigate the effect of spatial variability of unsaturated hydraulic conductivity on the movement of a nonreactive solute.

Several of these objectives will yield interpretations that are specific to the site. Even the site-specific results, however, will give valuable insight into the processes and properties that control flow and solute transport in the unsaturated zone. The results will also provide an opportunity to evaluate the accuracy of predictive modeling based on detailed measurements and field experimentation.

DESIGN OF THE FIELD EXPERIMENT

Test Plot

The field experiment was conducted at the Cape Cod site because much information about the structure and properties of the glacial outwash was available from previous studies. A large-scale, natural-gradient tracer test had been conducted at the site in 1985-88 to measure dispersivity in the saturated zone (LeBlanc and others, 1991). The spatial variability of hydraulic conductivity in the saturated zone had also been characterized in detail at a nearby site (Wolf, 1988; Hess, 1989). The infiltration test was run at a site about 60 m (meters) east of the multilevel-sampler array used during the large-scale tracer test and 90 m northeast of the area where saturated hydraulic conductivity had been measured in detail (fig. 1).

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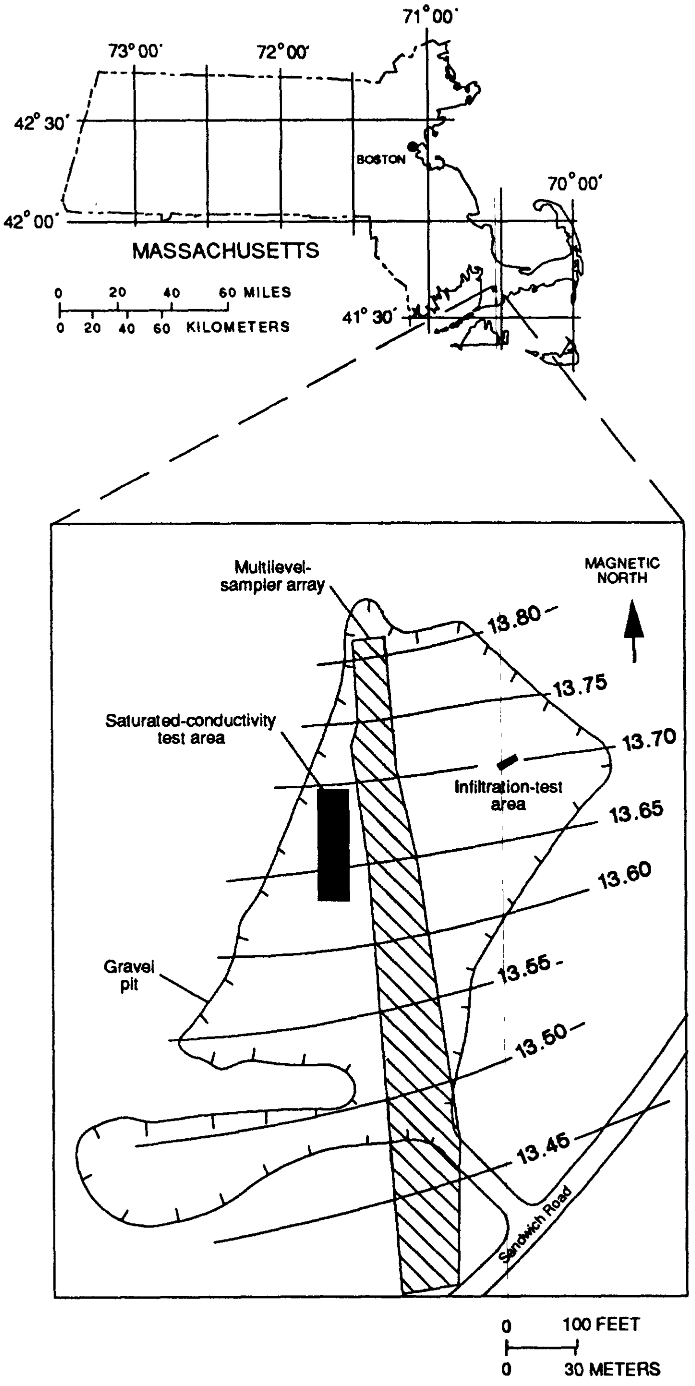
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72°00'
42°30'
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MASSACHUSETTS
0 20 40 60 MILES
0 20 40 60 KILOMETERS
41°30'
Multilevel-sampler array
MAGNETIC NORTH
13.80
13.75
Saturated-conductivity test area
13.70
Infiltration-test area
13.65
13.60
Gravel pit
13.55
13.50
13.45
Sandwich Road
0 100 FEET
0 30 METERS

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. Study area, showing location of irrigation-test plot, site of large-scale, natural-gradient tracer test, and site of drilling for measurement of hydraulic conductivity in the saturated zone.

The site was prepared by removing a 0.3-m-thick layer of disturbed surface soil. The undisturbed material beneath this layer is a medium to coarse sand and gravel that contains some cobbles but little silt and clay. In a trench dug adjacent to the test site (Hess and Wolf, 1991), the sand and gravel was observed to occur in layers that are several meters long and less than 0.5 m thick. The water table was about 6 m below ground surface.

Water flow and solute transport were monitored only in the top 2 m of the unsaturated zone. This interval was thick enough to represent the vertical variability of the sediments, but thin enough to be densely monitored because instrumentation could be installed easily to this depth. To permit adequate areal coverage by the instrument array, the overall test plot was 2 m wide and 10 m long (fig. 2); this area was large enough to locate the dense network of observation devices away from the edges of the irrigated area to minimize boundary effects.

Instrumentation

Instrumentation was installed in the unsaturated zone along the long centerline of the plot in 56 short rows that were spaced 12.5 cm (centimeters) apart. The total instrumented area was 0.5 m wide and 7.0 m long (fig. 2). Each row consisted of either time-domain reflectrometry (TDR) probes or suction-lysimeter/tensiometer devices installed to various depths. The type of device alternated from row to row.

The TDR probes in each row were installed in pairs to depths of 25, 50, 75, 100, 150, and 200 cm below ground surface (fig. 3). The probes, which are 4.8-millimeter-diameter steel rods, were driven in by hand. Pairs of probes were set at 10-cm intervals along a given row; the two probes in each pair were set 5.0 cm apart perpendicular to the rows. In the TDR method (Topp and others, 1980), an electromagnetic impulse is propagated along the wave guide provided by the pair of steel probes.

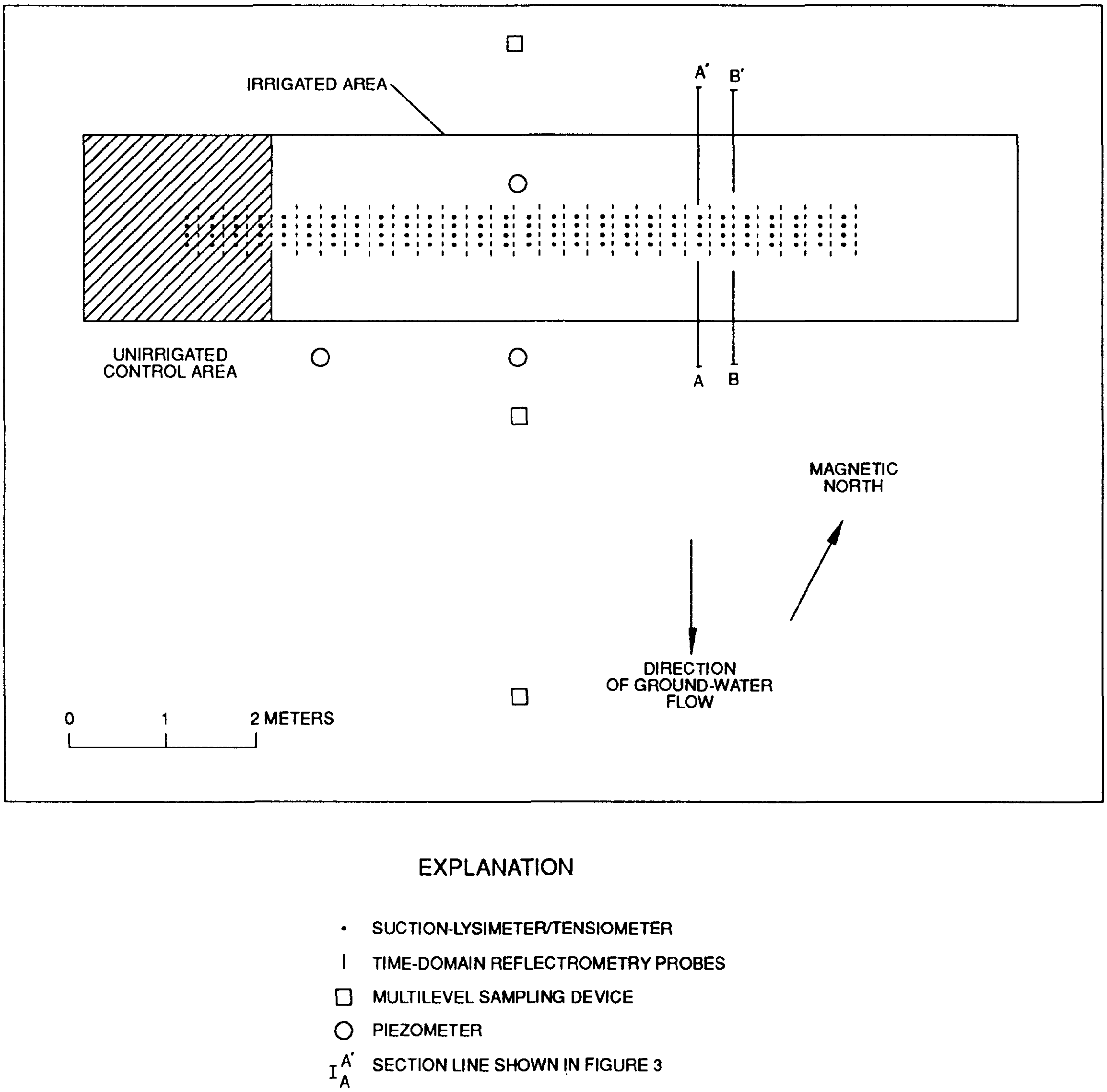
IRRIGATED AREA
A'
B'
UNIRRIGATED CONTROL AREA
A
B
MAGNETIC NORTH
DIRECTION OF GROUND-WATER FLOW
0
1
2 METERS
EXPLANATION
• SUCTION-LYSIMETER/TENSIOMETER
I TIME-DOMAIN REFLECTROMETRY PROBES
☐ MULTILEVEL SAMPLING DEVICE
○ PIEZOMETER
A' A SECTION LINE SHOWN IN FIGURE 3

Figure 2. Areal layout of infiltration-test experimental plot. Location of plot shown in figure 1.

The amplitude and attenuation of the reflected wave are related to the soil-moisture content and electrical conductivity of the bulk soil. Therefore, TDR was used to monitor soil-moisture content and solute-mass flux during the field tests.

The suction-lysimeter/tensiometers in each row were installed 10 cm apart to depths of 50, 100, 150, and 200 cm (fig. 3). These devices were installed by driving a 2.5-cm-diameter steel rod to the desired depth, removing the rod, and pushing the lysimeter/tensiometer into the hole. During various parts of the experiment, the devices were used as suction lysimeters to collect soil-moisture samples or as tensiometers to measure negative pressure (tension).

A plastic tarp covered 1.5 m of one end of the test plot to provide an unirrigated control area during the experiment (fig. 2). The unirrigated area included four rows of TDR probes and four rows of lysimeter/tensiometers.

Although the focus of the field tests was on flow and solute transport in the unsaturated zone, three piezometers were installed with screens at the water table to monitor the response of the water table to artificial recharge during the tests. In addition, three 15-port multilevel sampling devices were installed to observe tracer concentrations in the top 3.7 m of the saturated zone at 1 m upgradient and 1 and 4 m downgradient from the irrigated plot (fig. 2).

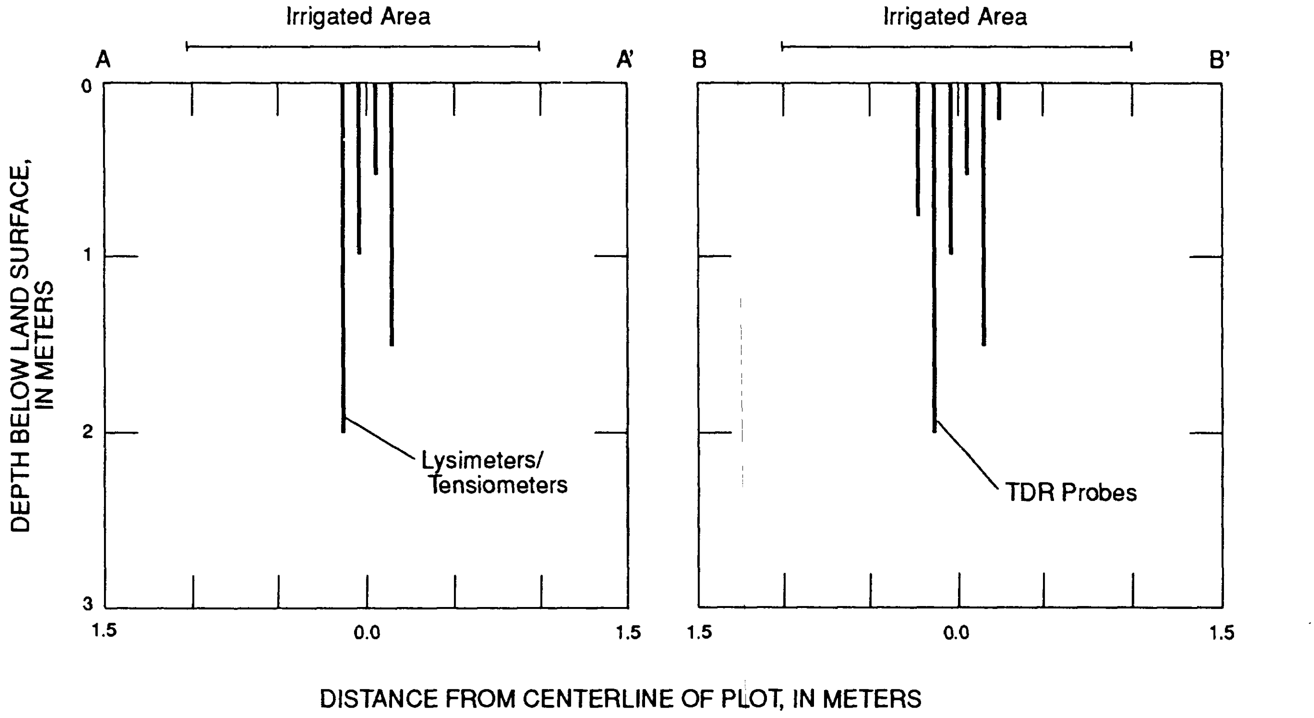

Figure 3. Vertical sections showing suction-lysimeter/tensiometers and time-domain reflectometry (TDR) probes. Lines of section shown in figure 2.

Irrigation System

The entire plot was covered with a tent to prevent recharge by precipitation and to minimize evaporation during the experiment. An irrigation system was set up to provide a uniform distribution of water over the 20-m^2 (square meter) plot at rates of 7.9 to 37.0 cm/h (centimeters per hour). This was accomplished by irrigation from 32 nozzles set 25 cm apart along the centerline of the plot and about 1.5 m above the ground surface. Water was supplied to the system from a shallow well located about 35 m east of the plot. Rainfall cups were used to check the rate and uniformity of irrigation. Despite the high irrigation rates, the infiltration capacity of the sand and gravel was not exceeded and overland flow did not occur. Solutes were added as an instantaneous pulse by hand irrigation with garden watering cans.

Irrigation Events

Two sets of tests were run during a 2-week-long period (table 1). The design of these runs, particularly the frequency of sample collection, was based on preliminary simulations with a one-dimensional numerical model of unsaturated flow and solute transport that used estimates of the hydraulic and transport characteristics of the site. During the first set, steady-state-flow and a steady soil-moisture content were established for four irrigation rates (7.9, 12.9, 24.8, and 37.0 cm/h). The purpose of these steady-state tests was to determine the average unsaturated hydraulic conductivity (equal to the irrigation rate) at various soil-moisture contents and to study the transport of solutes under different steady-flow conditions. The steady-flow conditions also allowed use of a new analytical method that estimates solute-mass flux from the attenuation of the TDR signal (Kachanoski and others, in press).

For each rate, the plot was irrigated until the TDR measurements for all depths indicated that soil-moisture content was constant and steady-state conditions had been reached. The tracer solution was then added to the plot over a very brief interval (usually less than 30 seconds) and irrigation was continued. The tracer was chloride, a nonreactive solute, added as sodium chloride at a rate of 100 grams of chloride per square meter of irrigated area (except for run 1; see table 1). To obtain this application rate, 1 liter of tracer solution with a chloride concentration of 100 grams per liter was applied uniformly to each square meter of irrigated area. After application of the tracer solution, TDR monitoring continued and collection of water samples from the suction lysimeters began. Monitoring and collection of samples continued until the solute pulse passed completely below the 2-m maximum depth of the instrumentation.

During the first set of tests, the response of the water table to artificial recharge was observed in the three piezometers. Water samples were collected intermittently from the multilevel sampling devices to record the time of arrival and subsequent rate of movement of the tracer in the saturated zone.

The purpose of the second set of tests was to observe transient variations in pressure and soil-moisture content during several wetting and drying cycles (table 1). The suction lysimeters were converted to tensiometers by filling the porous cups with water prior to the start of this set; thus, pressure measurements could be made with a field pressure meter to minimize the measurement response time to pressure changes. The TDR measurements were used to observe the advance of the wetting front during irrigation. For each cycle, measurements of pressure and soil-moisture content were made most frequently during the period shortly after a change in irrigation rate when these variables were expected to change most rapidly. For two cycles, irrigation was followed by a drying period during which drainage was allowed to occur. For one cycle, the irrigation rate was increased without an intervening drainage period.

Table 1. *Summary of irrigation tests run during July 1990 field experiment*

[Cm/h, centimeter per hour; g/m^2, gram per square meter of irrigated area; --, not available; N/A, not applicable]

Run	Flow condition	Date	Irrigation rate, cm/h	Tracer mass, g/m^2	Local time (24-hour clock) Start irrigation	Add tracer	Stop irrigation	Drainage time prior to irrigation, hours
1	Steady	07/10/90	12.9	75.3	--	1730	2400	N/A
2	Steady	07/12/90	24.8	100.0	0730	1100	1630	N/A
3A	Steady	07/12/90	37.0	100.0	1630	1930	2150	N/A
3B	Steady	07/13/90	37.0	100.0	0915	1315	1600	N/A
4	Steady	07/17/90	7.9	100.0	0700	1030	2100	N/A
1M	Transient	07/18/90	7.9	N/A	1610	N/A	2120	19.2
2M	Transient	07/19/90	24.6	N/A	0950	N/A	1425	12.5
3M	Transient	07/19/90	36.8	N/A	1425	N/A	1830	0

PLANS FOR DATA ANALYSIS AND FURTHER RESEARCH

The large amount of data collected during the field tests is presently being compiled and entered into computer files. In addition, approximately 12,000 water samples are being analyzed for chloride concentration.

For each test in the first set, which focused on solute transport, the steady-state soil-moisture content will be obtained from the TDR data, and the average unsaturated hydraulic conductivity will be estimated from the irrigation rate. The results from the four irrigation rates will be used to examine the relation of average unsaturated conductivity to average moisture content. The TDR data will be interpreted to obtain estimates of solute-mass flux, which will be further analyzed to obtain solute-breakthrough curves at the TDR locations. The breakthrough curves will be used to examine local and transect-averaged longitudinal dispersion of solutes and to estimate the distribution of solute concentrations at given times during the test. The accuracy of the TDR-derived solute concentrations will be assessed by comparing these values to chloride concentrations measured directly in the suction-lysimeter water samples.

For the second set of tests, pressures from the tensiometers and soil-moisture contents from the TDR will be used to generate pressure/saturation curves through the sampled space. These small-scale results can be used to estimate an average functional relation between moisture content and pressure for the test site.

Plans for further analysis include an evaluation of the spatial variability of flow and solute-transport properties and their effect on the observed soil-moisture contents and solute distributions. This variability will be compared to the variability measured in the saturated zone during earlier studies. To improve understanding of the complex processes of flow and solute transport, the tests will be simulated with numerical models. The ability of the models to predict flow and solute transport in the unsaturated zone using data sets which are much more comprehensive than are obtained in typical field studies will also be examined.

This work may be supplemented by additional field work in the next year. The additional work may include the collection of cores from the test plot for laboratory analysis of grain size and pressure/saturation response. A trench may also be dug through the test plot to observe the stratigraphy directly.

This experiment focused on a two-dimensional vertical section of the aquifer and examined transport of only a nonreactive tracer. Despite this focus, the effort was not trivial. The results of this experiment will be used to plan field experiments that examine the three-dimensional nature of flow and solute transport in the unsaturated zone. Future experiments may also be designed to address the fate of reactive solutes that are important environmental contaminants, such as agricultural chemicals.

SUMMARY

An infiltration experiment was conducted at the Cape Cod site in July 1990 to examine flow and solute transport in the unsaturated zone of a sand and gravel glacial outwash. The objectives of the experiment were to test new field methods to measure flow and transport in the unsaturated zone and to improve understanding of unsaturated-zone hydrology in heterogeneous sediments. The experiment involved irrigation of a densely instrumented 20-m^2 plot and observation of soil-moisture content, pressure, and tracer concentrations. Instrumentation included 168 pairs of time-domain-reflectrometry probes and 112 suction-lysimeter/tensiometers installed to depths of 25 to 200 cm below ground surface. Two sets of tests were run during a 2-week-long period. The first set focused on transport and dispersion of chloride, a nonreactive tracer, under steady-state flow at four irrigation rates. The second set focused on unsteady flow and the corresponding response of hydraulic properties during several wetting and drying cycles.

This experiment focused on a two-dimensional vertical section of the aquifer. It also examined only transport of a nonreactive tracer. This focus was chosen to test data-collection and analysis methods in this hydrogeologically heterogeneous setting within a reasonable time and budget.

The results of this experiment will be used to plan field experiments that examine the three-dimensional nature of flow and solute transport in the unsaturated zone. Future experiments may also be designed to address the fate of reactive solutes that are important environmental contaminants, such as agricultural chemicals. These experiments will be linked to the development of mathematical models that simulate this complex system and can be used jointly with field experiments to improve our ability to predict the movement and fate of contaminants in the subsurface.

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SIMULATION OF MOLYBDATE SORPTION WITH THE DIFFUSE LAYER SURFACE-COMPLEXATION MODEL

By Kenneth G. Stollenwerk[1]

ABSTRACT

Sorption of molybdate [Mo(VI)] as a function of aqueous and solid phase composition was evaluated in laboratory experiments. Sorption of Mo(VI) decreased as pH, sulfate (SO_4), and phosphate (PO_4) increased. Sorption of Mo(VI) increased with ferrihydrite content. Experimental data could be quantitatively modeled with the diffuse-layer surface-complexation model in the geochemical equilibrium speciation model MINTEQA2. Intrinsic acidity constants and intrinsic equilibrium constants for PO_4 sorption were obtained from the sorption literature. Intrinsic equilibrium constants for Mo(VI) and SO_4 were fit to experimental data: for Mo(VI), $LogK2^{int} = 8.0$ and $LogK3^{int} = -1.0$; for SO_4, $LogK2^{int} = 5.0$ and $LogK3^{int} = -0.4$. One set of equilibrium constants was used to simulate the experimental sorption data for the entire range of geochemical conditions that were considered.

INTRODUCTION

Several different models can be used to describe sorption of solutes at mineral surfaces. Empirical models like the distribution coefficient and Freundlich isotherm are mathematically simple and readily incorporated in solute-transport codes; however, empirical models commonly are applicable only to a limited range of geochemical conditions. Sorption is affected by changes in the composition of aqueous solutions, and the number of parameters needed to describe sorption isotherms becomes too large for empirical models. Surface-complexation models presume a mechanistic explanation of sorption reactions and can simulate sorption in complex geochemical systems.

Surface-complexation models treat the chemical reactions at the solid-solution interface as surface complexation reactions analogous to the formation of complexes in solution. Each reaction is defined in terms of a thermodynamic equilibrium constant. Several surface-complexation models have been described in the literature. All are based on electric double-layer theory but differ in their geometric description of the oxide/water interface and the treatment of the electrostatic interactions. Thorough reviews of surface-complexation theory and the various models that have been developed were recently published (Davis and Kent, 1990; Dzombak and Morel, 1990).

This paper describes the application of a surface complexation model to simulate sorption of Mo(VI) measured in laboratory experiments. The experiments were designed to provide information on the processes that controlled transport of Mo(VI) in a large-scale, natural-gradient tracer test. The tracer test was conducted on Cape Cod, Mass. (fig. 1) to examine the transport and dispersion of solutes in a sand and gravel aquifer. Details of the tracer test are described in LeBlanc and others (1991).

METHODS

Experimental

Batch experiments were used to evaluate the effects of changes in solution composition and sediment type on Mo(VI) sorption. Ground water and sediment collected from the tracer test site were used in all experiments. Composition of the ground water used in these experiments (table 1) represents the range in chemical constituents measured in the aquifer during the tracer test. Ground water in the upper part of the aquifer (from well F347-20) consists of freshwater recharge and is low in dissolved solids and pH. Dissolved solids and pH increase with depth as a result of mixing with a plume of sewage-contaminated ground water (from well F347-46) (fig. 1).

Columns of sediment were preleached with the ground water used in a particular experiment. After the sediment was dried, 30 grams were mixed in polyethylene centrifuge tubes with 30 milliliters of ground water to which differing concentrations of Mo(VI), SO_4, or PO_4 had been added. Acid or base was added to maintain the desired pH. The mixtures were equilibrated for 7 days on a rotating mixer at 0.8 revolutions per minute. Solutions were separated by filtration (0.4 micrometer) and analyzed for Mo(VI) by a modification of the thiocyanate colorimetric procedure (Barasko, 1967). Sulfate and PO_4 were analyzed by ion chromatography. Ferrihydrite and crystalline iron oxide content of core samples were determined by sequential extraction (Chao and Zhou, 1983). The pH and concentration of Mo(VI), SO_4, PO_4, and ferrihydrite were varied in individual experiments as follows:

(1) Sorption of Mo(VI) as a function of pH at two different concentrations of SO_4 and PO_4. Intrinsic equilibrium constants for Mo(VI) and SO_4 were adjusted to fit these experimental data.

(2) Aqueous concentration of SO_4 and PO_4 was varied.

(3) Mo(VI) concentration was varied; pH, SO_4 and PO_4 were held constant.

(4) Mo(VI) sorption at two different ferrihydrite concentrations.

Geochemical Modeling

Experimental results were modeled with the diffuse-layer surface-complexation model contained in MINTEQA2 (Allison and others, in press). MINTEQA2 is a geochemical equilibrium speciation model that offers the

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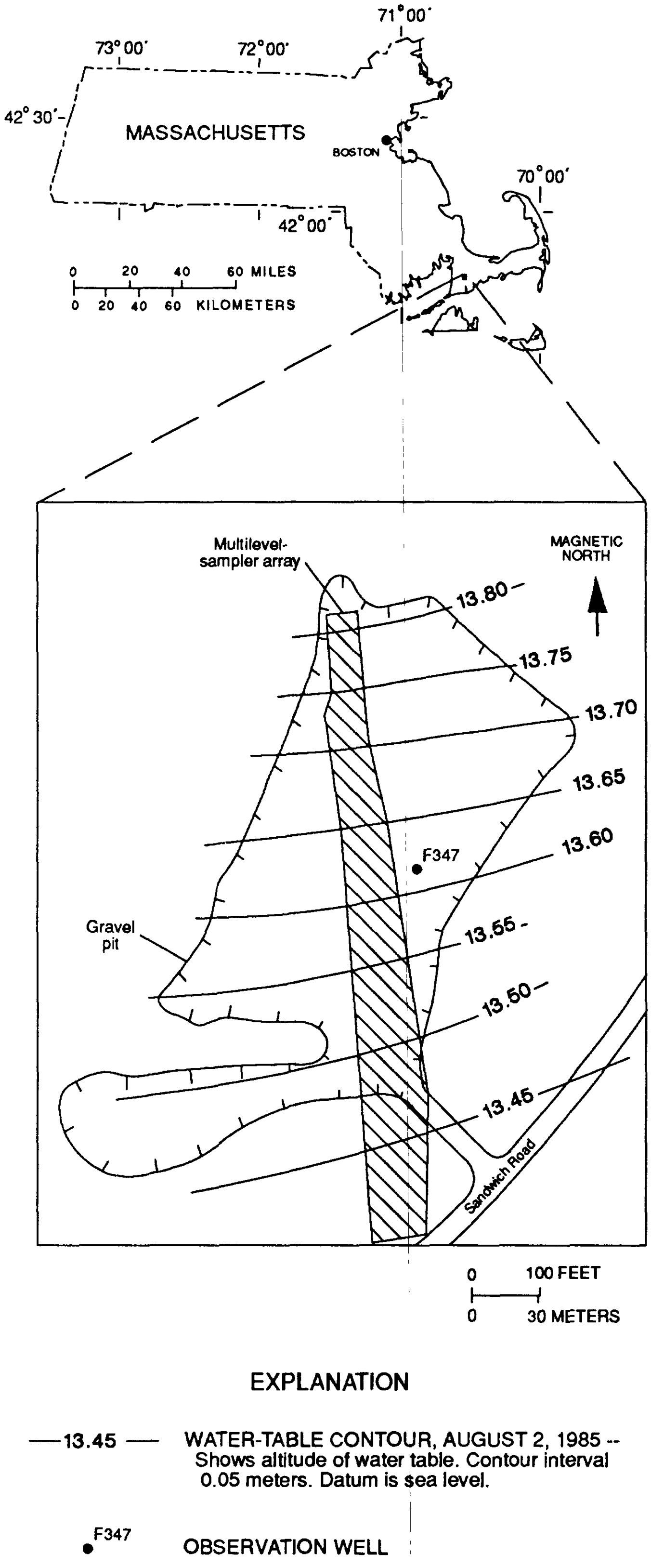
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Sandwich Road
0 100 FEET
0 30 METERS
EXPLANATION
13.45 WATER-TABLE CONTOUR, AUGUST 2, 1985 -- Shows altitude of water table. Contour interval 0.05 meters. Datum is sea level.
F347 OBSERVATION WELL

Figure 1. Location of large-scale natural-gradient tracer test. (Modified from LeBlanc and others, 1991.)

Table 1. *Composition of ground water used in batch experiments*

[mmol/L, millimoles per liter; <, below detection]

Ground water	Concentration (mmol/L)									
	Ca	Mg	Na	K	Cl	SO_4	HCO_3	NO_3	PO_4	pH
F347-20	0.020	0.029	0.17	0.01	0.14	0.086	0.080	<	<	5.64
F347-46	.21	.14	1.7	.1	.82	.45	1.3	.19	.016	6.43

Table 2. *Sorption constants for the diffuse layer model*

[m^2/g, square meters per gram; mol/mol Fe, moles sorption sites per mole iron; $LogK^{int}$, log of the intrinsic surface complexation constant; $\equiv FeOH^0$, ferrihydrite surface complexation site]

Ferrihydrite properties

Percent ferrihydrite in sediment, average - 0.015; range, 0.012-0.036
Specific surface area - 600 m^2/g[1]
Concentration of sorption sites - 0.2 mol/mol Fe[1]

Surface-complexation reactions	$LogK^{int}$	
	Dzombak and Morel[1]	Experimental
(1) $\equiv FeOH^0 + H^+ = \equiv FeOH_2^+$	$LogK_{a1}^{int}$ = 7.29[2]	
(2) $\equiv FeOH^0 = \equiv FeO^- + H^+$	$LogK_{a2}^{int}$ = -8.93[2]	
(3) $\equiv FeOH^0 + 3H^+ + PO_4^{3-} = \equiv FeH_2PO_4^0 + H_2O$	$LogK_1^{int}$ = 31.39[2]	
(4) $\equiv FeOH^0 + 2H^+ + PO_4^{3-} = \equiv FeHPO_4^- + H_2O$	$LogK_2^{int}$ = 25.39[2]	
(5) $\equiv FeOH^0 + H^+ + PO_4^{3-} = \equiv FePO_4^{2-} + H_2O$	$LogK_3^{int}$ = 17.72[2]	
(6) $\equiv FeOH^0 + H^+ + MoO_4^{2-} = \equiv FeMoO_4^- + H_2O$	$LogK_2^{int}$ = 9.5	8.0[2]
(7) $\equiv FeOH^0 + MoO_4^{2-} = \equiv FeOHMoO_4^{2-}$	$LogK_3^{int}$ = -2.4	1.0[2]
(8) $\equiv FeOH^0 + H^+ + SO_4^{2-} = \equiv FeSO_4^- + H_2O$	$LogK_2^{int}$ = 7.78	5.0[2]
(9) $\equiv FeOH^0 + SO_4^{2-} = \equiv FeOHSO_4^{2-}$	$LogK_3^{int}$ = -0.79	-0.4[2]

[1]Dzombak and Morel, 1990.

[2]Constants used in model simulations.

choice of four empirical sorption models and three surface-complexation models. Thermodynamic data for solid and aqueous phases of molybdenum, compiled by Kaback and Runnells (1980), were added to the thermodynamic database of MINTEQA2.

MINTEQA2 requires that the user define the surface complexation reactions and sorption properties of the mineral phases. Ferrihydrite and goethite are the most reactive oxide minerals in sediment from the tracer test site. Although goethite was more abundant than ferrihydrite in sediment, the surface area and concentration of sorption sites is much greater in ferrihydrite. To simplify computations, sorption reactions were assumed to occur only on ferrihydrite. Sorption properties of ferrihydrite are listed in table 2.

Phosphate and SO_4 competed with Mo(VI) for sorption sites and were included in the diffuse-layer model. A total of nine surface complexation reactions were required to model the experimental data (table 2). Intrinsic equilibrium constants for reactions 1 to 5 are from Dzombak and Morel (1990), and are based on an extensive compilation of experimental data for pure ferrihydrite systems. Equilibrium constants from Dzombak and Morel (1990) for reactions 6 to 9 were used initially, and then sequentially adjusted to obtain the best fit to experimental data. The constants in table 2 were used to model all experimental data.

RESULTS

Experiment 1

Sorption of Mo(VI) was found to be highly dependent on pH, ranging from almost complete sorption to very little sorption over a range of 2.5 pH units (fig. 2). The difference in the amount of Mo(VI) sorbed between the two sets of experimental data was assumed to be caused by increased competition for sorption sites from the greater concentrations of SO_4 and PO_4 in the sewage contaminated ground water (F347-46, table 1) compared to uncontaminated ground water (F347-20, table 1).

The diffuse-layer model overestimated the amount of Mo(VI) sorbed when the $LogK^{int}$ values for Mo(VI) and SO_4 from Dzombak and Morel (1990) (table 2) were used. These constants were extrapolated from experimental data for relatively pure ferrihydrite. Oxides coating the surfaces of sediment used in this study are most likely a mixture of

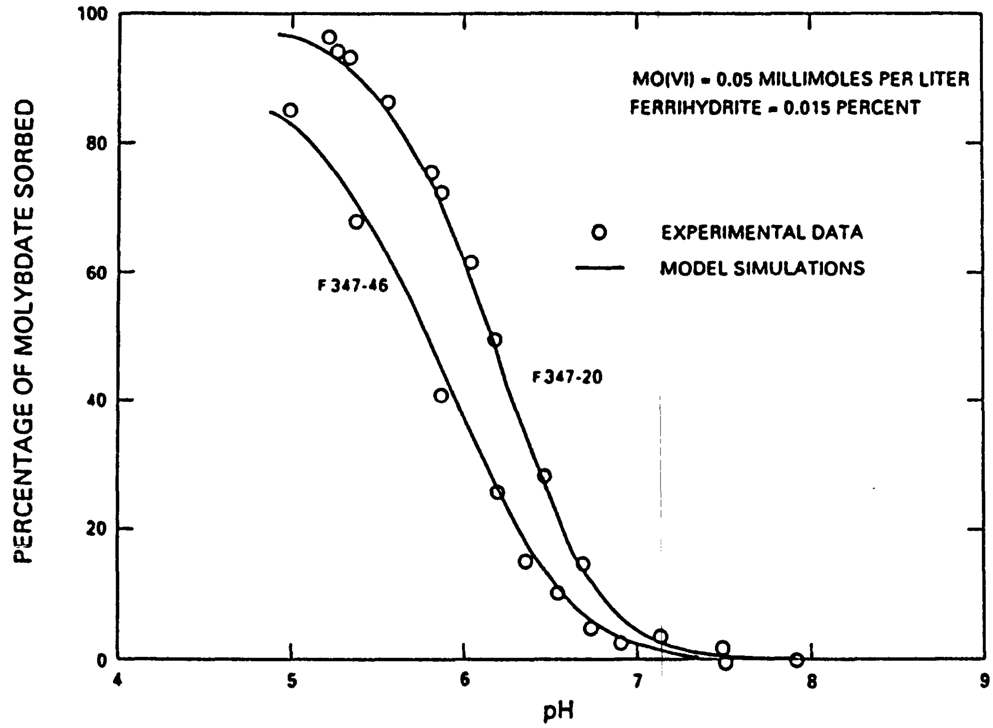

Figure 2. Measured and modeled effect of pH on sorption of Mo(VI) in water from wells F347-20 and F347-46.

minerals, for example, MnO_2 and $Fe(OH)_3$. The experimental $LogK^{int}$ values (table 2) may represent such a mixture. Empirical $LogK^{int}$ values were able to fit the experimental data over the entire pH range (fig. 2).

Experiment 2

Sulfate has a much smaller effect on sorption of Mo(VI) than does PO_4 (fig. 3). In this set of experiments, pH and the initial aqueous concentration of Mo(VI) were constant, and the concentration of SO_4 or PO_4 was varied. As the ratio of SO_4 to Mo(VI) changed from 0.2 to 50, the amount of Mo(VI) sorbed decreased from 50 to 40 percent; whereas, the amount sorbed decreased from 47 to almost 0 percent for the same range of PO_4/Mo(VI). The intrinsic equilibrium constants from experiment 1 described the effect of anion competition on Mo(VI) sorption reasonably well.

Experiment 3

Sorption of Mo(VI) also is a function of aqueous Mo(VI) concentration. Constant pH isotherms for Mo(VI) sorption are plotted in figure 4. Isotherms were generated by varying the initial aqueous concentration of Mo(VI) at each pH. Experimental data exist for pH 6.1, 6.3, and 6.5. There is a linear relation between the concentration sorbed and in solution at low aqueous concentrations. The linear part of each isotherm can be simulated with the empirical Freundlich equation:

$$\bar{c} = K_f c^n ,$$

where $\bar{c}$ is the concentration of Mo(VI) sorbed, in millimoles per kilogram; K_f is the Freundlich adsorption equilibrium constant, in liters per $kilogram^{-n}$; c is the concentration of Mo(VI) in solution, in millimoles per liter; and n is the Freundlich exponent (slope of line on a log plot of $\bar{c}$ as a function of c.

However, a different value of K_f would be required to fit the sorption isotherms for each pH value. Also, any significant change in SO_4 or PO_4 would affect the value of K_f and n. Thus, simulation of Mo(VI) transport in the tracer test would require a continuum of Freundlich sorption constants that bracketed the geochemical variability of the aquifer. The diffuse-layer model, although more complex mathematically, has the capability of simulating sorption in a complex geochemical system with one set of constants.

Experiment 4

The concentration of sorption sites in the aquifer is a function of the ferrihydrite content of the sediment. The ferrihydrite content of 60 sediment samples from 4 cores collected adjacent to the tracer-test area ranged from 0.012 to 0.036 percent and averaged 0.015. Experimental data for Mo(VI) sorption on sediment that contained 0.012 and 0.036 percent ferrihydrite are plotted in figure 5. The difference in sorption between the two core samples was proportional to the number of sorption sites, and could be simulated by the diffuse layer model.

SUMMARY

The diffuse-layer surface-complexation model coupled with the aqueous geochemical speciation program

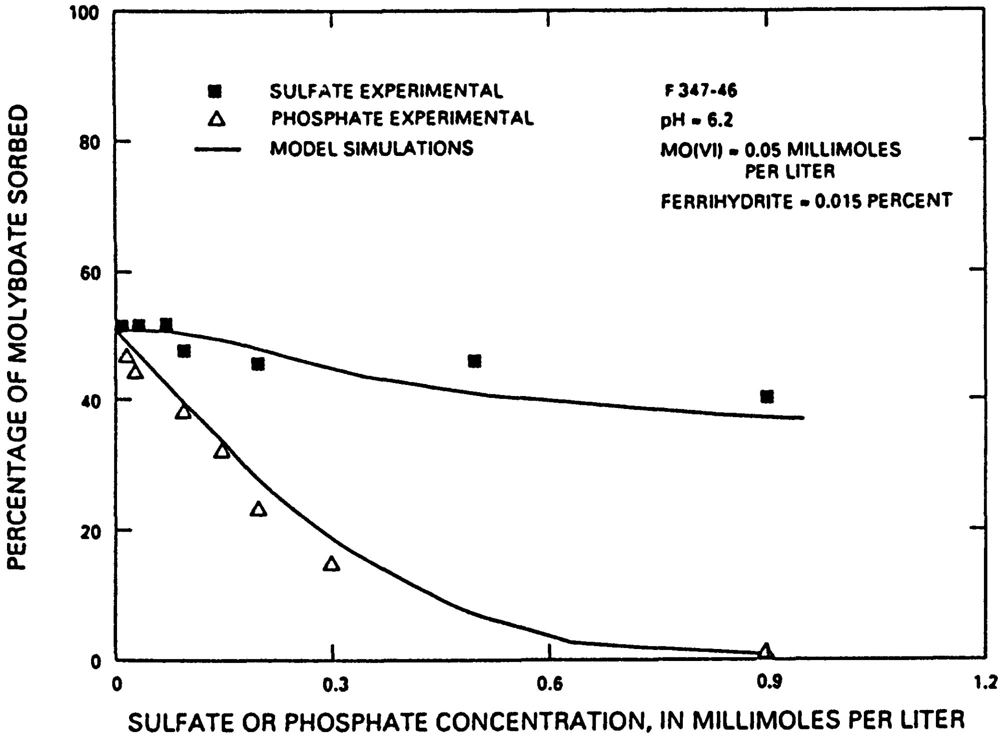

Figure 3. Measured and modeled effect of SO4 and PO4 competition on sorption of Mo(VI) in water from well F347-46.

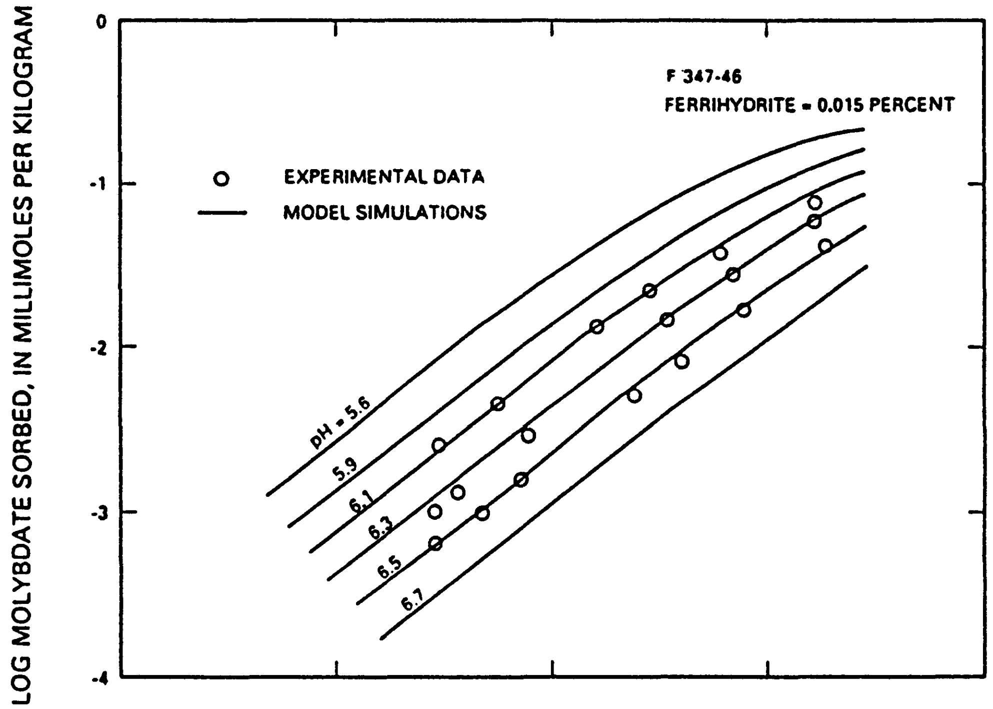

Figure 4. Measured and modeled effect of pH on sorption of Mo(VI) in water from well F347-46.

MINTEQA2 was used to simulate sorption of Mo(VI) by natural aquifer materials in laboratory experiments. Sorption was a function of the ferrihydrite content of the sediment, pH, SO4, PO4, and Mo(VI) concentration. Nine equations were required to describe the significant sorption reactions at the oxide/water interface. One set of equilibrium constants for all nine reactions was used to model the entire range of geochemical properties evaluated in the laboratory experiments.

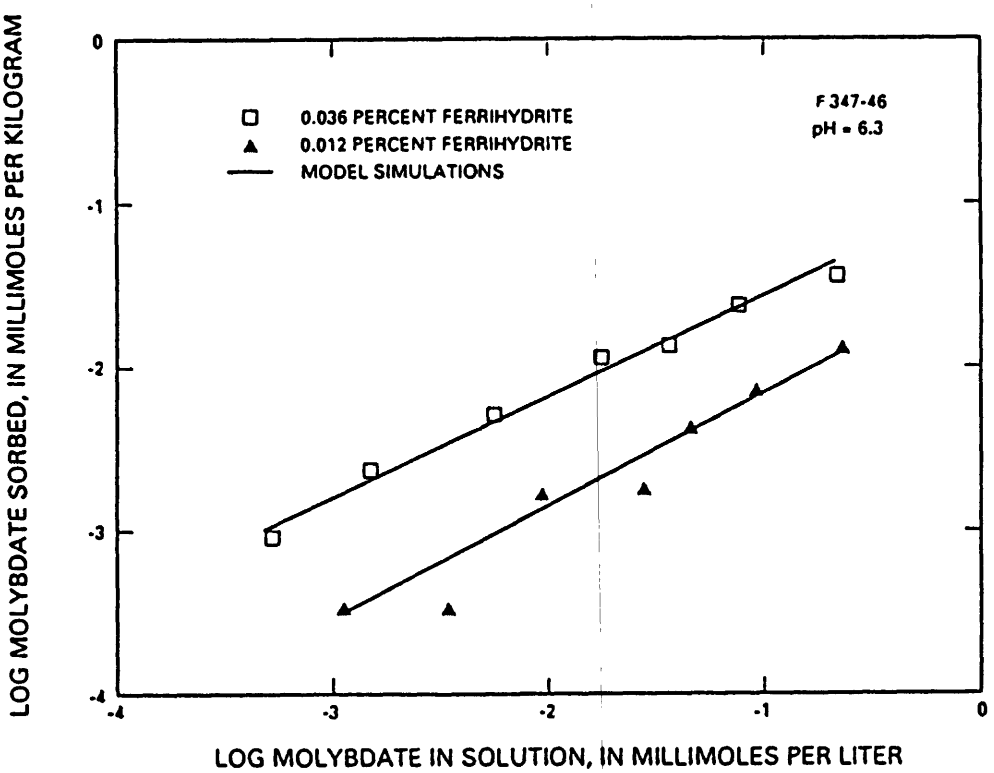

Figure 5. Measured and modeled effect of ferrihydrite concentration on sorption of Mo(VI) in water from well F347-46.

Surface acidity constants and intrinsic equilibrium constants for PO_4 sorption were obtained from the geochemical literature and are based on experimental data for pure ferrihydrite systems. Intrinsic equilibrium constants for Mo(VI) and SO_4 sorption were empirically fit to the experimental data in this study. For Mo(VI), $\mathrm{LogK2}^{\mathrm{int}} = 8.0$, and $\mathrm{LogK3}^{\mathrm{int}} = -1.0$. For SO_4, $\mathrm{LogK2}^{\mathrm{int}} = 5.0$, and $\mathrm{LogK3}^{\mathrm{int}} = -0.4$.

The surface-complexation-model approach to the simulation of sorption reactions can be a valuable aid to solute-transport modeling of natural systems where complex geochemical interactions preclude the use of mathematically simple empirical models such as the Freundlich isotherm. For best results, the surface-complexation models should be part of a geochemical speciation program so that other reactions also can be evaluated. A major disadvantage is the significant increase in computer time required to do the chemical and transport calculations.

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EFFECT OF THE GEOCHEMICAL ENVIRONMENT ON HEAVY-METAL TRANSPORT IN GROUND WATER

By J.A. Davis[1], D.B. Kent[1], B.A. Rea[1], Stephen P. Garabedian[2], *and* L.D. Anderson[1]

ABSTRACT

An overview is presented of a field-based research program that is examining the significance of chemical reactions in heavy-metal transport in ground water. Both natural-gradient tracer tests and laboratory experiments with subsurface materials are being used to evaluate the relative importance of hydrologic and geochemical processes affecting metal transport. The experiments are being conducted in an uncontaminated recharge zone and in sewage-contaminated zones of the sand and gravel aquifer at the Cape Cod Toxic-Substance Hydrology Research Site. The results of tracer tests with zinc, chromium, and selenium showed that various chemical processes can have a dominant effect on metal transport; these processes include oxidation-reduction, adsorption-desorption, and aqueous complexation reactions. In some cases, significant speciation changes occurred as the injected tracers moved downgradient, and the changes generally had marked effects on the reactivity of the tracers with the porous medium. The experiments revealed that equilibrium geochemical models will be difficult to apply in modeling the transport of some redox-sensitive contaminants, such as chromium(VI) and selenium(VI), because of the specific nature of interactions of each element with reductants. A practical modeling approach for describing metal transport in ground water may require laboratory experiments designed specifically to identify and minimize the number of chemical reactions considered in a hydrogeochemical transport model.

INTRODUCTION

Contamination of ground water by metal ions may occur as a result of improper operation or inappropriate design of municipal or industrial landfills, disposal of liquid or solid mining wastes or mill tailings, or ineffective containment of nuclear wastes. Quantitative assessment of hazards or risks arising from such contamination requires a fundamental understanding of the mechanisms governing transport, including chemical, physical, and biological processes. Among the important chemical processes that affect the transport of metal ions are complexation reactions in water and reactions that result in the removal of metal ions from water, for example, adsorption and precipitation. Most metal ions that are toxic are also strongly adsorbed by the surfaces of minerals in aquifers, although their reactivity depends on the particular mineral assemblage and the composition of the ground water (Davis and Kent, 1990). The formation of an aqueous complex can have a significant effect on the tendency of a metal ion to adsorb (Hsi and Langmuir, 1985). When strongly complexed, a metal ion may be transported downgradient at an average velocity that is orders of magnitude faster than would be expected in the absence of the ligand. For example, field studies have shown that radionuclides may be mobile in ground water when complexed with organic ligands (Cleveland and Rees, 1981; Killey and others, 1984). The ligand may be present naturally (fulvic acid or carbonate anions) or may be introduced as a contaminant. Changes in speciation, and therefore reactivity, can result from encountering different chemistries along a ground-water flow path. Another significant factor that may affect metal transport is the redox environment of ground water (Liu and Narasimhan, 1989). Many elements may exist in more than one oxidation state, for example, arsenic, chromium (Cr), copper, iron (Fe), mercury, manganese (Mn), molybdenum, selenium (Se), uranium, vanadium, and the actinide elements. The mobilities of the different oxidation states of these metals may differ by orders of magnitude.

We are using both field- and laboratory-scale experiments to study the transport of metals that undergo changes in speciation (and reactivity) involving complexation, adsorption, and electron-transfer reactions. Our objectives are to identify important processes affecting metal transport, to examine the relation between chemical and physical factors affecting transport, and to stimulate the development of hydrogeochemical models that can predict the transport of metal ions in field settings. Natural-gradient tracer tests are being conducted in oxic and suboxic zones of the aquifer at the Cape Cod Toxic-Substances Hydrology Research Site (CCTSHRS), using bromide (Br), zinc (Zn), nickel (Ni), lead (Pb), Cr, Se, and EDTA (a metal complexing agent) as tracers. The hypothesis is that the effect of hydrologic processes can be separated from chemical and microbial processes by comparing the transport of Br (a nonreactive tracer) with that of the other tracers. Furthermore, the influence of aquifer chemistry, in particular, the redox environment, can be examined by comparing the results of tracer tests in the oxic and suboxic zones of the aquifer. In this paper, we summarize the objectives of our ongoing research activities at the site and describe the methods used and the major geochemical and hydrologic features of the ground-water system. Only a brief summary of results is presented. More detailed results are presented in five separate papers in this Proceedings: Anderson and others (1991) (Cr(VI) mobility in the oxic, recharge zone), Davis, Waite, Kent, and Anderson (1991) (Cr(VI) mobility in the suboxic, sewage-contaminated zone), Fuller and others (1991) (spatial heterogeneity of geochemical and hydrologic parameters), Kent and others (1991) (mobility of Zn-EDTA complexes in tracer tests), and Rea and others (1991) (mobility of Zn in the sewage plume).

FIELD SITE DESCRIPTION

Tracer-injection tests were carried out in the shallow, unconfined sand and gravel aquifer at CCTSHRS, near Falmouth, Mass. (fig. 1). The upper 30 m (meters) of the

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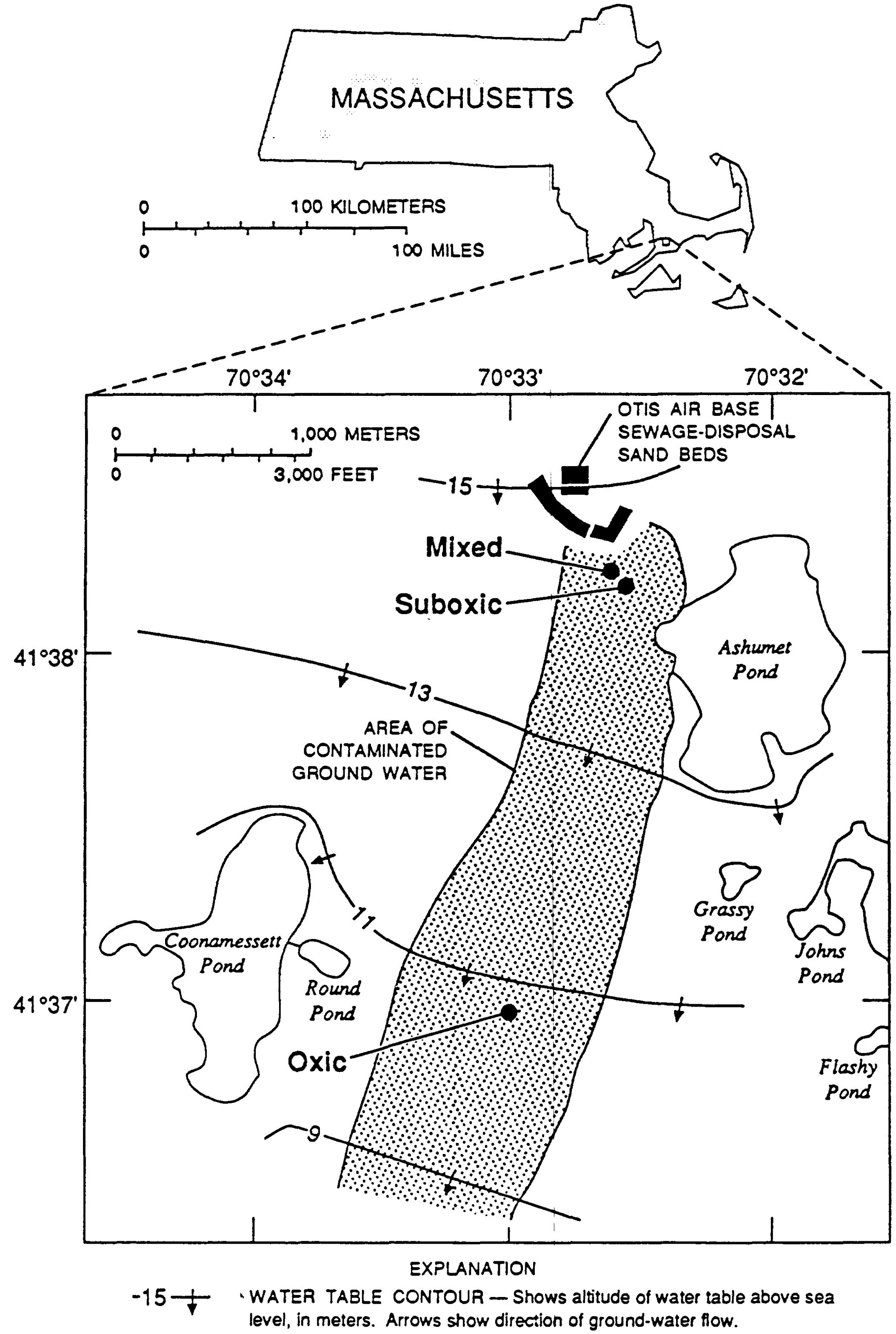
MASSACHUSETTS
0
100 KILOMETERS
0
100 MILES
70°34'
70°33'
70°32'
0
1,000 METERS
0
3,000 FEET
OTIS AIR BASE
SEWAGE-DISPOSAL
SAND BEDS
15
Mixed
Suboxic
41°38'
13
Ashumet
Pond
AREA OF
CONTAMINATED
GROUND WATER
11
Grassy
Pond
Coonamessett
Pond
Round
Pond
Johns
Pond
41°37'
Oxic
Flashy
Pond
9
EXPLANATION
-15
WATER TABLE CONTOUR — Shows altitude of water table above sea level, in meters. Arrows show direction of ground-water flow.

Figure 1. Location of field sites for natural-gradient tracer tests in a shallow sand and gravel aquifer at the U.S. Geological Survey Cape Cod Toxic-Substances Hydrology Research Site near Falmouth, Massachusetts. The oxic site (site O) designates where a tracer test was conducted in the recharge zone. The suboxic and mixed sites (sites S and M) designate the locations of tests in the suboxic, sewage-contaminated zone. At the mixed site, ground water from the recharge zone at the oxic site was injected with tracers into the suboxic zone.

aquifer are a permeable, stratified, sand and gravel outwash (LeBlanc, 1984). Beneath the outwash, the sediments are a fine-grained sand and silt. The median grain size of the outwash is about 0.6 millimeters, and it generally contains less than 1 percent silt and clay by weight (Barber, 1987). Quartz, plagioclase, and orthoclase consititute about 90 percent by weight of the minerals; the remaining 10 percent consists of biotite, hornblende, muscovite, and other accessory minerals typically associated with glacial outwash derived from source rocks of granitic composition (Barber, 1987). The hydrologic characteristics of the site are summarized in LeBlanc and others (1991).

The locations of the tracer-injection tests are shown in figure 1. We shall refer to the locations of the separate tests as O for oxic, M for mixed, and S for suboxic. Two of the experiments (at sites M and S) were conducted within an array of densely instrumented multilevel ground-water samplers (MLS) used in a previous large-scale tracer test (LeBlanc and others, 1991). This array of samplers (more than 600) is located about midway between the Otis Air Base sewage-disposal site and Ashumet Pond, a kettle-hole pond in the outwash plain (fig. 1). A third experiment was conducted at site O, approximately 2.3 km (kilometers) downgradient from sites M and S, where an additional small array of MLS was installed. Disposal of treated sewage to the aquifer at Otis Air Base has caused the formation of a contaminant plume that underlies the test sites (fig. 1). The plume is about 23 m thick and more than 4 km long. A zone of uncontaminated, aerobic ground water, derived from precipitation, overlies the plume. Between the two zones is a transition zone, varying in thickness from 1 to 3 m, containing sharp gradients in the concentrations of dissolved salts, dissolved oxygen (DO), and nitrate and in pH. General aspects of the water composition of the uncontaminated and contaminated zones are summarized by LeBlanc and others (1991).

The distribution of injected tracers in the aquifer was monitored by collection of water samples using the arrays of MLS. Each MLS consists of 15 color-coded polyethylene tubes (0.47 cm (centimeter) inside diameter). The cluster of tubes runs from land surface down the inside of a polyvinyl chloride casing, and then out holes drilled at various depths (see LeBlanc and others, 1991). The open, downhole end of each tube is screened with a fine nylon fabric. The vertical spacing between sampling ports is generally constant for a given MLS, but ranges from 25.4 cm to 50.8 cm for the MLS used in this study. Each tube of the MLS can be sampled by suction from land surface using a peristaltic pump. Sufficient water was pumped from the tubes to purge the tube three times before collecting samples for anion (unacidified) and metal (acidified) analysis.

Background Chemistry and Design of Field Experiments

The recharge zone contains uncontaminated, oxic water with approximately 250 μM (micromolar) DO 8 ppm (parts per million), low pH (4 to 5), and low concentrations of dissolved salts (specific conductance of 30 μS/cm (microsiemens per centimeter)). The sewage-contaminated zone is nearly anoxic (referred to here as suboxic, see below), containing DO concentrations less than 10 ppb (parts per billion)) and dissolved Mn(II) in concentrations as high as 10 μM (550 ppb). This zone has a higher pH (6.5-7.0) and higher conductance (350-400 μS/cm) than the recharge zone. Dissolved Fe(II) was occasionally present above the detection limit (50 ppb), but was found only at a few points in the part of the sewage plume that is sampled by MLS. When found, the presence of Fe(II) was usually distinct but localized, with concentrations often exceeding 20 μM (1.12 ppm) when Fe(II) was detected. However, Fe(II) concentrations were usually very low in sampling ports adjacent, above, and below any points at which it was found at elevated concentrations. Gschwend and Reynolds (1987) reported an Fe(II) concentration of 190 μM (10.6 ppm) in a 5 cm diameter well (F343-57) located about 20 m upgradient from site M. That well is screened over a 60 cm interval that is several meters below the bottommost tube of the MLS at site M.

Dissolved sulfide concentrations were below detection (50 ppb) in both zones, and the dissolved methane concentration is less than the concentration expected for equilibrium with the atmosphere (Smith and others, 1989). Dissolved organic carbon concentrations are 0.3 mg/L (milligrams per liter) in the recharge zone and 2 to 4 mg/L in the sewage-contaminated zone (Barber and others, 1988). The sewage effluent had a dissolved organic carbon concentration of 11 mg/L during sampling in 1983 and 1985.

Figures 2, 3, and 4 illustrate some of the chemical characteristics of the ground water at sites M, S, and O, respectively, before the tracer tests were conducted. Figures 2 and 3 show the gradients with depth of pH, specific conductance (shown as K), and dissolved calcium (Ca), Mn, and DO concentrations in the sewage-contaminated zones at sites M and S. The uppermost tubes of these MLS are located at depths within or near the recharge zone, but most of the tubes sample from the sewage-contaminated zone. The nitrate profiles at these sites (data shown for site S only) show sharp increases within the transition zone and top of the sewage zone (Smith and others, 1991), but then decrease substantially to near zero at the center of the sewage-contaminated zone (fig. 3). Very low concentrations of DO (6 ppb, 0.2 μM) in the sewage zone have been measured with a special MLS constructed with copper tubing located near site S (R.L. Smith, U.S. Geological Survey, oral commun., 1989). Measurements of DO - concentrations in the sewage zone using MLS with polyethylene tubing consistently yielded values of 100 to 200 ppb (3 - 6 μM). However, these values were in error, due to permeation of oxygen through the walls of the tubing in the vadose zone (approximately 6 m in thickness). The zinc concentration profile at site M shown in figure 2 results from contamination of the aquifer by sewage and is discussed in more detail by Rea and others (1991, this Proceedings).

The thickness of the recharge zone increases with distance downgradient from the Otis Air Base sewage disposal site as the sewage plume sinks (LeBlanc, 1984). The recharge zone within the densely-instrumented array of MLS at sites M and S is only about 2 m thick or less (figs. 2 and 3). Because it was desired to conduct one of the tracer tests under oxic conditions, a small array of MLS was installed at site O, where the recharge zone is much thicker

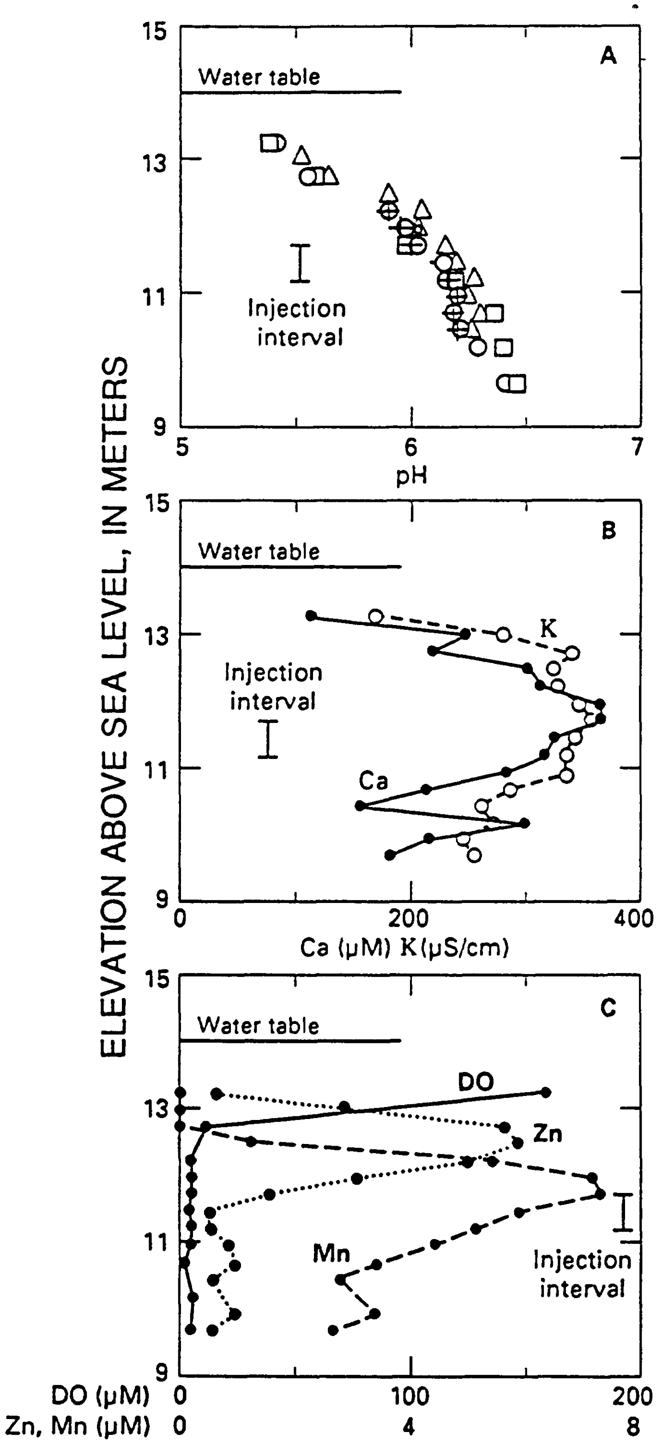

Figure 2. Vertical profile of pH, specific conductance (shown as K), and dissolved oxygen (DO), calcium (Ca), zinc (Zn), and manganese (Mn) concentrations at the mixed site (site M) before tracer tests were conducted. A: circles, pH at multilevel sampler 10-15 , April 1988; squares, pH at multilevel sampler 12-11, April 1988; triangles, pH at multilevel sampler 10-16, July 1988; + signs, pH at multilevel sampler 10-15, July 1988. B: Data from multilevel sampler 10-15 in April 1988. C: Data from multilevel sampler 10-15 in July 1988.

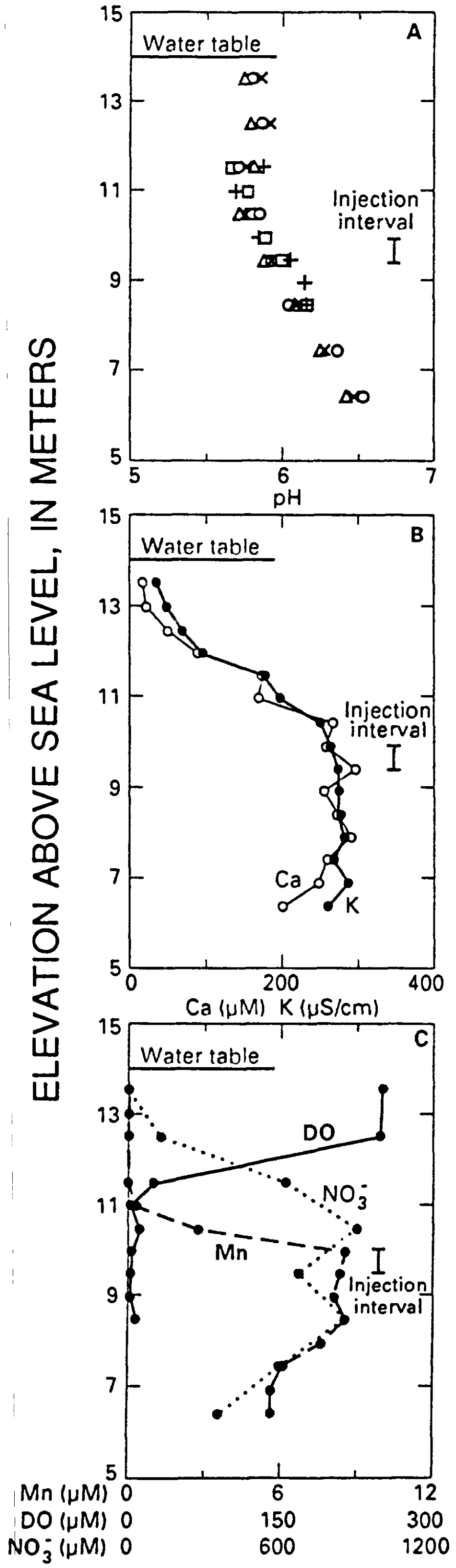

Figure 3. Vertical profile of pH, specific conductance (shown as K), and dissolved oxygen (DO), calcium (Ca), manganese (Mn), and nitrate (NO_3^-) concentrations at the suboxic site (site S). A: Triangles, X's, pH at multilevel sampler 38-12, April 1988; circles, pH at multilevel sampler 37-12, April 1988; + signs, pH at multilevel sampler 37-12, July 1988. B: Data from multilevel sampler 37-12, April 1988. C: All data from multilevel sampler 37-12: manganese, April 1988; dissolved oxygen concentration were identical in April 1988 and September 1989; nitrate, September 1989.

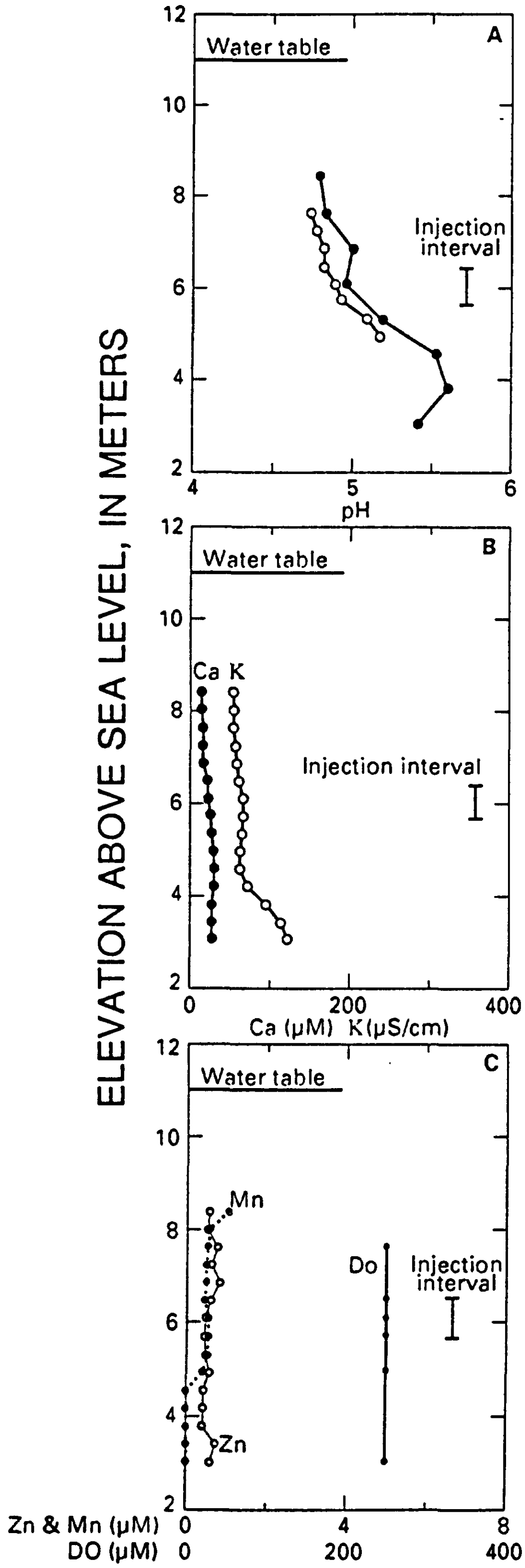

Figure 4. Vertical profile of pH, specific conductance (shown as K), and dissolved oxygen (DO), calcium (Ca), zinc (Zn), and manganese (Mn) concentrations at the oxic site (site O) before tracer tests were conducted. A: Filled circles, pH, April 1988; open circles, pH, July 1988. B: Data from April 1988. C: Data from April 1988.

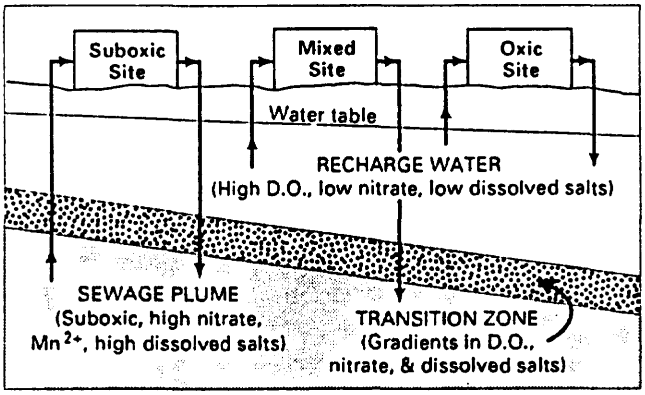
Suboxic Site
Mixed Site
Oxic Site
Water table
RECHARGE WATER
(High D.O., low nitrate, low dissolved salts)
SEWAGE PLUME
(Suboxic, high nitrate, Mn2+, high dissolved salts)
TRANSITION ZONE
(Gradients in D.O., nitrate, & dissolved salts)

Figure 5. Schematic diagram showing recharge and sewage-contaminated zones of the shallow aquifer and the zones used for withdrawing and injecting ground water for the three natural-gradient tracer tests conducted in July 1988.

(about 6 m). Most of the tubes of the MLS at this site sample water from the recharge zone, although water from the bottom tubes showed increases in specific conductance (fig. 4), perhaps indicating the top of the transition zone. The pH increases with depth from values of 4.65 at the top tube to 5.5 at the bottom tubes.

Three natural-gradient tracer tests were initiated in July 1988; each was characterized by a different set of conditions with respect to dissolved oxygen concentration. At the oxic site (O), recharge water was withdrawn, mixed with the tracers, and pumped back into the recharge zone at the same depth interval (fig. 5). At the suboxic site (S), the same type of experiment was conducted with suboxic water. At the mixed site (M), oxic recharge water was mixed with the tracers and then pumped into the suboxic zone (fig. 5). Approximately 380 L (liters) of ground water was withdrawn for each tracer test from either two or three tubes of an MLS into an acid-washed polyethylene bag containing the tracers (as salts), and this spiked water was then pumped back into the same tubes from which ground water was withdrawn (except for the mixed site, explained below). The tracers and their concentrations are shown in table 1. Breakthrough of the tracers was monitored at several MLS downgradient from the injection MLS. Br was used as a nonreactive tracer of the injected water. EDTA was added to enhance the transport of Zn. EDTA may be specifically involved in the transport of metals in some contaminated ground waters (Jacobs and others, 1988). However, its use here was solely to serve as a general model for complexing ligands and their role in enhancing metal transport.

Table 1. *Concentrations of tracers added to ground water*

Tracers	Concentration (millimolar)
KBr	1.9
K_2H_2EDTA	.5
$Zn(NO_3)_2{\cdot}6H_2O$	.1
K_2CrO_4	.1
Na_2SeO_4	.06

Oxic Site (Site O)

The MLS designated as F168-M1 was used for the experiment conducted with recharge water, initiated on July 9, 1988. Three tubes (vertical separation of 0.38 m) were used to collect ground water characterized by oxic conditions, low pH (5.1), and low concentrations of background salts. The vertical interval used for sampling ground water and injecting the tracers is indicated in figure 4. The ground water was withdrawn by peristaltic pump, thoroughly mixed with the tracers in the polyethylene bag, and pumped back into the aquifer (see fig. 5) at a rate of 2 L/min (liters per minute) (0.67 L/tube/min (liter per tube per minute)).

The Suboxic Site (Site S)

MLS 37-12 (see Garabedian and others, 1988) for a description of MLS numbering) was used to conduct a tracer experiment within the sewage-contaminated zone, commencing on July 10, 1988. Two tubes (vertical separation of 0.51 m) were used to collect ground water characterized by very low concentrations of DO, pH (6.1), and greater concentrations of background salts than found in the recharge water (fig. 3). The water contained 8 μM dissolved Mn but no detectable Fe(II), indicating mildly reducing conditions. The vertical interval for ground-water withdrawal and tracer injection is indicated in figure 3. The ground water and tracers were mixed in the polyethylene bag after it had been purged twice with nitrogen. The water contained about 800 ppb (25 μM) DO when it was reinjected with the tracers at 2 L/min (1 L/tube/min).

The Mixed Site (Site M)

MLS 10-15 was used to conduct a tracer test begun on July 8, 1988, in which oxic recharge water with tracers was injected into the sewage-contaminated zone (see fig. 5). The same three tubes at site O that were employed subsequently (on July 9, 1988) for the oxic injection were used to withdraw oxic water from the recharge zone. The oxic water was mixed thoroughly with the tracers in the polyethylene bag and then was transported to site M, where it was pumped into three tubes (vertical separation of 0.25 m, interval shown in fig. 2) located within the suboxic sewage-contaminated zone. In addition to the difference in DO concentration, the injected water contained lower concentrations of major salts, for example, sulfate, calcium, than the ambient ground water.

OVERVIEW OF RESULTS

Zinc Mobility

Important changes in metal speciation may occur along a ground-water flow path, as solutes in a waste discharge mix with ambient ground water or encounter different geochemical regimes downgradient. The physical processes that lead to fluid mixing and macrodispersion may affect aqueous speciation of metal ions by dilution of complexing ligands or the addition of new solutes from dissolving mineral phases. Zn^{2+}, as a free cation, may adsorb extensively onto minerals present in the porous medium (Benjamin and Leckie, 1981; Zasoski and Burau, 1988). The $ZnEDTA^{2-}$ complex may also adsorb, but it is expected to be considerably more mobile, based on a study of $CdEDTA^{2-}$ mobility in a sandy aquifer (Fuller and Davis, 1987). Changes in the distribution of dissolved zinc between Zn^{2+} and the $ZnEDTA^{2-}$ complex can result from dispersion-induced dilution of EDTA or competition for EDTA between Zn^{2+} and other cations (for example, Fe, Mn, and Ca). Such changes in aqueous speciation would be expected to affect the mobility of Zn.

Adsorption-desorption processes and complexation reactions were found to have a significant effect on the transport of Zn in the natural-gradient tracer tests conducted at CCTSHRS (Kent and others, 1991, this Proceedings). Significant speciation changes occurred as Zn moved downgradient, and the speciation of Zn had a marked effect on its reactivity with the porous medium. In the uncontaminated recharge zone, retardation of Zn transport (relative to Br) was caused by its displacement from Zn-EDTA complexes by Fe(III) dissolved from minerals in the porous medium (Kent and others, 1991, this Proceedings). In contrast, the $ZnEDTA^{2-}$ complex was transported nearly conservatively within the sewage-contaminated zone. In this zone, Zn^{2+} was desorbed from subsurface material by the excess injected EDTA, suggesting that a large reservoir of adsorbed zinc is present in the aquifer as a result of sewage contamination (Rea and others, 1991, this Proceedings).

Chromium Mobility

The concept of redox reaction sequences, with distinct redox zonation, has proven useful in modeling the evolution of ground-water quality along a subsurface flow path (Back and Baedecker, 1989). Each redox zone is dominated by a particular redox reaction. The sequence of redox zones observed is explained in terms of a model in which organic matter is oxidized by the oxidant yielding the greatest free energy change per mole of organic carbon oxidized (Berner, 1981). When this oxidant is depleted, oxidation will proceed utilizing the next most efficient oxidant, until all oxidants are consumed or oxidizable organic matter is depleted. Organic matter is usually assumed to be the only electron donor. Thus, oxygen is first consumed, then manganese oxides and nitrate are reduced, iron oxides are reduced, sulfates are reduced, and finally methane is produced. In the case of ground-water contamination by an organic-rich discharge, the redox zones are usually observed to occur in a lateral sequence along a ground-water flow path downgradient from the source (Baedecker and Back, 1979).

The redox status at sites M and S within the sewage-contaminated zone is poised at mildly reducing, suboxic conditions. At the elevations sampled by the MLS, the conditions appear to fall between the oxic and iron-rich (postoxic) classes of redox status given by Berner (1981), in that the water is characterized by very low concentrations of dissolved oxygen, yet contains very little Fe(II). Smith and

Duff (1988) have shown that the rate of denitrification in the sewage-contaminated zone is limited by the availability of organic carbon. Thus, the sequence of redox zonation processes appears to have advanced only to the stage of partial denitrification and manganese reduction (figs. 2 and 3) in the aquifer near sites M and S. Almost all dissolved oxygen has been consumed in the sewage-contaminated plume before the ground water reached sites M and S. The presence of high concentrations of Fe(II) observed by Gschwend and Reynolds (1987) suggests that the redox status may be characterized by more reducing conditions in sections of the sewage plume at lower elevations or further upgradient toward the sewage infiltration beds.

Little is known about the manner in which sequential redox zones affect the transport of redox-sensitive metal contaminants, such as Cr and Se (Stollenwerk and Grove, 1984). Cr(VI) is rapidly reduced to Cr(III) by Fe(II) in circumneutral solutions (Eary and Rai, 1988). This reaction effectively limits the transport of chromium in iron-rich reducing ground waters, because Cr(III) is very strongly sorbed by mineral surfaces and is of limited solubility at pH values greater than 6 (Sass and Rai, 1987; Schultz and others, 1987). In addition to reduction by dissolved Fe(II), Cr(VI) may be reduced by the surfaces of mineral phases containing Fe(II), such as biotite or magnetite (White, 1990), especially in acidic water. Cr(VI) may also be reduced by rapid reactions with dissolved or detrital organic material, for example, oxalic acid, lactic acid, and various other carboxylic acids, alcohols, and aldehydes (Benson, 1976). The reduction of Cr(VI) by less reactive organic matter may be catalyzed by bacteria in either aerobic or anaerobic environments, in which Cr(VI) is used as a terminal electron acceptor (Komori and others, 1989).

It is instructive to compare the equilibrium constants of redox half- reactions to see what might be expected for Cr and Se in such a mildly reducing environment. Table 2 shows the values of effective equilibrium constants for several important redox half-reactions at pH 6, a typical value for the sewage-contaminated zone at sites M and S. Each reaction is normalized for the exchange of one electron, and the equations are positioned in order of decreasing equilibrium pe_{eff} at pH 6. Thus, in theory, any reductant on the right-hand side of the equation is thermodynamically capable of reducing any oxidant on the left-hand side that is higher up in the table (see Morel, 1983). Se(VI) reduction (to elemental Se) (see Oremland and others, 1989) and Cr(VI) reduction occur at nearly the same pe_{eff}, after the consumption of nitrate and manganese oxides, but before the reduction of iron hydroxide. Because nitrate has not been fully consumed within the section of the sewage plume at sites M and S, a chemical equilibrium model of redox zonation would predict that Cr and Se would not be reduced under these conditions, inasmuch as the pe_{eff} represented by nitrate reduction is too oxidizing.

In dilute aqueous solutions, Cr(VI) exists primarily as chromate (CrO_4^{2-}) and bichromate ($HCrO_4^-$) anions. In addition to the reduction process described above, Cr mobility may be affected by adsorption of these anions. Cr(VI) is weakly adsorbed by the surfaces of many oxide minerals, especially iron and aluminum oxides (Zachara and others, 1987; Davis and Kent, 1990).

Results of tracer injection tests conducted at sites M, S, and O in 1988 and 1989 show that Cr(VI) is reduced to Cr(III) in both the suboxic and oxic zones of the aquifer, and Cr(III) was irreversibly sorbed in each zone (see Anderson and others, 1991, this Proceedings; Davis, Waite, Kent, and Anderson, 1991, this Proceedings). Cr(VI) adsorption was observed only within the recharge zone of the aquifer, where low pH and low ionic strength conditions are favorable for its adsorption (Zachara and others, 1987). In each case, the transport of Cr was greatly affected by chemical processes other than advection and dispersion. For example, in the suboxic zone, Cr transport was attenuated, but not retarded (by attenuation we mean that the total mass of Cr being transported was decreased). The attenuation was caused by irreversible sorption of Cr(III). The Cr was transported only as Cr(VI), and no retardation was observed because of insignificant Cr(VI) adsorption in this zone. The reduction of Cr(VI) appeared to be an abiotic process (Davis, Waite, Kent, and Anderson, 1991, this Proceedings). In the oxic recharge zone, Cr transport was both retarded and attenuated, because of irreversible sorption of Cr(III) and reversible adsorption of Cr(VI). The results suggest that the chemical equilibrium model of redox zonation may not adequately describe the role of redox processes in governing the transport of Cr(VI).

In contrast, Se(VI) was not reduced in the suboxic zone and was transported conservatively (Davis, Kent, Rea, Maest, and Garabedian, 1991). Abiotic reduction of Se(VI) is known to be slow and microbial catalysis of the reduction apparently did not occur, perhaps due to inhibition by nitrate (Oremland and others, 1989). In the recharge zone, Se(VI) transport was retarded by reversible adsorption onto the porous medium, due to the favorable conditions of low pH and low ionic strength (Davis, Kent, Rea, Maest, and Garabedian, 1991).

Spatial Variability of Adsorptive Reactivity

The most common inorganic adsorbents of metal ions in geological materials are the hydrous metal oxides (as discrete minerals or as coatings), carbonates, clays, and sands, whereas the most common organic adsorbents consist of detrital plant material and humic coatings on mineral surfaces (Davis and Kent, 1990). Many studies of metal adsorption onto geological materials have concluded that iron and manganese hydrous oxides and organic materials are the predominant adsorbents, although Fuller and Davis (1987) showed that calcite dominated the adsorption of Cd^{2+} by an aquifer sand. Among the inorganic adsorbents, hydrous metal oxides may have the highest affinity for metal ions because of their charged, reactive hydroxyl groups, combined with their high specific surface area (Davis and Kent, 1990).

When considering equilibrium adsorption processes, solute-transport models require the knowledge of adsorption constants, and either adsorbent surface areas or mineral abundances, in order to quantify the interactions between dissolved metals and adsorbing surfaces of the porous medium. It has been presumed that these adsorption parameters can be adequately determined in the laboratory through batch or column studies with materials collected from a field site. However, any spatial variability of the mineral assemblage and

Table 2. *Effective equilibrium constants for selected redox reactions at pH 6.0*

Equation	pe °[1]	pe_{eff} (pH=6)
$\frac{1}{4}O_2(g) + H^+ + e^- = \frac{1}{2}H_2O$	20.75	14.75
$\frac{1}{5}NO_3^- + \frac{6}{5}H^+ e^- = \frac{1}{10}N_2(g) + \frac{3}{5}H_2O$	21.05	13.85
$\frac{1}{2}MnO_2(s) + 2H^+ + e^- + \frac{1}{2}Mn^{2+} + H_2O$	20.8	8.8
$\frac{1}{2}NO_3^- + e^- = \frac{1}{2}NO_2^- + \frac{1}{2}H_2O$	14.15	8.15
$\frac{1}{6}SeO_4^{2-} + \frac{4}{3}H^+ + e^- = \frac{1}{6}Se(s) + \frac{2}{3}H_2O$	14.8	6.8
$\frac{1}{3}HCrO_4^- + \frac{7}{3}H^+ + e^- = \frac{1}{3}Cr^{3+} + \frac{4}{3}H_2O$	20.2	6.2
$\frac{1}{2}O_2(g) + H^+ + e^- = \frac{1}{2}H_2O_2$	11.5	5.5
$Fe(OH)_3(s) + 3H^+ + e^- = Fe^{2+} + 3H_2O$	16.0	-2.0
$\frac{1}{8}SO_4^{2-} + \frac{5}{4}H^+ + e^- = \frac{1}{8}H_2S(g) + \frac{1}{2}H_2O$	5.25	-2.25
$\frac{1}{4}HCO_3^- + \frac{5}{4}H^+ + e^- = \frac{1}{4}$ "CH_2O" $+ \frac{1}{2}H_2O$	[2]1.8	[3]-5.7

[1] Constants from Morel[106].

[2] Based on "CH_2O" equal to one sixth of a glucose molecule.

[3] Based on the activity of bicarbonate ion equal to 1 millimolar.

its associated surface coatings may make it difficult to collect a representative sample of aquifer material that would reflect the adsorption behavior of a metal ion over the large travel distances of interest in field applications. An analogous conceptual problem exists in describing the spatial variability of hydraulic conductivity, and this problem has been intensively studied by Hess (1989) at CCTSHRS.

The spatial variability of grain size distribution, metal adsorption coefficients, and other geochemical parameters is being determined in 16 cores of subsurface material collected at the site (Fuller and others, 1991, this Proceedings). The hydraulic conductivity at CCTSHRS can be estimated from the grain size distribution of the material (Wolf, 1988). The results of this work will be used in conjunction with metal injection studies (Kent and others, 1991, this Proceedings) to develop a field-oriented approach for modeling toxic metal transport in ground water.

CONCLUDING REMARKS

Considerable progress has been made by other research groups in the development of theoretical solute-transport models and associated computer codes that couple reactions with ground-water flow (Rubin, 1990). A few of these models include the consideration of adsorption processes, but there is a general lack of appreciation of the importance of water composition and metal speciation in regulating the adsorption of metal ions, and hence, in affecting their mobilities in ground water. Empirical models that employ partition coefficients or isotherms are of limited utility in describing metal adsorption if the water chemistry of an aquifer is variable (Reardon, 1981; Davis and Kent, 1990), a condition frequently found in waste discharge applications. A more fundamental, mechanistic approach that uses the surface ionization and coordination concept in conjunction with aqueous speciation models is now widely accepted for modeling the adsorption of metal ions with mineral surfaces. To date, only Cederberg and others (1985) have incorporated this type of approach within a hydrogeochemical transport model, although other models could be adapted to this approach with a limited number of reactions (Rubin, 1990).

A general, but practical, modeling approach is urgently needed for realistic descriptions of metal transport at contaminated field sites. A strategy needs to be formulated that minimizes the number of chemical and microbiological processes that are coupled with a flow model in specific applications, to reduce computational requirements. Tracer-injection tests and laboratory experiments with subsurface materials can isolate the chemical reactions of importance in specific geochemical settings, thereby minimizing the number of reactions that must be considered. Such tests can reveal the specific nature of chemical reactions involving subsurface materials and redox-sensitive contaminants, such as Cr and Se, that may be difficult to predict from equilibrium geochemical models. The major ions dissolved in ground water may affect the adsorptive reactivity of trace contaminants, for example, Cr(VI), and thus, the processes controlling the concentrations of the major ions may also need to be considered in some applications. In addition, this field-based approach can identify microscale, nonequilibrium processes that are likely to be significant in describing the transport of contaminants, such as diffusion into secondary matrix porosity (Wood and others, 1990) or Cr(VI) reduction under oxic conditions (Anderson and others, 1991, this Proceedings).

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ADSORPTION AND REDUCTION OF CHROMIUM(VI) UNDER OXIC CONDITIONS IN A SHALLOW SAND AQUIFER AT CAPE COD, MASSACHUSETTS

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ABSTRACT

Investigations of chromium transport in both oxic and suboxic ground water have been carried out at the U.S. Geological Survey Cape Cod Toxic-Substances Hydrology Research site. The results of tracer injection studies indicate that reduction and adsorption of chromium(VI) occurred during transport in the oxic zone but only reduction occurred in the suboxic zone. Batch experiments with freshly collected core material and recharge water substantiated reduction by the sands from the oxic zone. Reductive potential was substantially reduced in air-dried sands from both the oxic and suboxic zones, probably as a result of oxidation of organic material or the surfaces of ferrous-containing minerals. The major part of removal on air-dried oxic core sands was reversible and was less intense in the presence of increased sulfate. These results suggested that the reversible reaction was adsorption of chromium(VI). Adsorption on air-dried sand from the suboxic zone was weak (less than 12 percent for recharge water and less than 5 percent in sewage-contaminated water). Chromium(VI) reduction occurred on the air-dried sands but it was substantially less than fresh core material. Total amount of reduction was dependent on pH but independent of solution composition and whether the sand was collected from the oxic or suboxic zone.

INTRODUCTION AND BACKGROUND

Aquifer chemistry plays an important role in the transport of chromium (Cr) in ground water (Davis, Kent, Rea, Maest, and Garabedian, 1991). Laboratory studies with synthetic and natural solids have demonstrated that the reactivity of Cr is strongly dependent on the speciation. Cr(VI) is present in natural waters as the weakly adsorbing anions $HCrO_4^-$ and CrO_4^{2-}. Adsorption of Cr(VI) on minerals decreases with increasing pH and increasing concentration of other anions such as sulfate (for example, Leckie and others, 1984; Zachara and others, 1987). Cr(III) is strongly adsorbed or precipitated at pH values greater than 4 (Leckie and others, 1984; Rai and others, 1987). Reduction of Cr(VI) to Cr(III) can occur under a variety of conditions (even in the presence of dissolved oxygen) if a suitable electron donor is present. Reducing agents include aqueous iron (Fe)(II), Fe(II) at mineral surfaces, and a variety of organic compounds (Eary and Rai, 1989; White, 1990; Fish, 1991).

Investigations of Cr transport in ground water have been carried out at the U.S. Geological Survey Cape Cod Toxic-Substances Hydrology Research site (CCTSHRS) (fig. 1). Disposal of treated sewage effluent to ground water at the Otis Air Base sewage treatment facility has resulted in an extensive plume of sewage-contaminated ground water. The sewage plume underlies a zone of recharge water that is derived from precipitation. This juxtaposition gives rise to strong vertical gradients in the chemical composition of the ground water (Smith and others, 1991). The recharge zone is oxic, has pH values in the range of 4.5 to 5.5, and has low concentrations of dissolved salts (conductivity is about 50 μS/cm (microsiemens per centimeter)). The sewage plume is suboxic, with dissolved oxygen concentrations at or below 0.2 mM (millimolar), pH of about 6.5, and higher concentrations of dissolved salts (conductivity is about 375 μS/cm (see Davis, Kent, Rea, Maest, and Garabedian, 1991 for a detailed description of ground water chemistry in the vicinity of the investigations described herein).

Cr transport is expected to be different in the two chemically distinct zones. The low pH and concentration of dissolved salts in the recharge zone provide conditions favorable for adsorption and, therefore, retardation of Cr(VI). Higher pH and dissolved salts within the sewage plume will be less favorable to Cr(VI) adsorption, whereas the mildly reducing conditions in the sewage plume will increase the likelihood of reduction of Cr(VI) to Cr(III). Cr(III) should be immobilized and, thus, reduction of Cr(VI) to Cr(III) would lead to a decrease in Cr mass transport relative to a nonreactive tracer. Reduction of Cr(VI) to Cr(III) could also occur in the oxic (recharge) zone if reactive reducing agents are present.

In this paper, we report preliminary results of Cr transport under oxic conditions. Cr transport under suboxic conditions is disussed in an accompanying paper (Davis, Waite, Kent, and Anderson, 1991, this Proceedings). Cr transport was studied with small-scale, natural-gradient tracer tests at the CCTSHRS. The chemical processes controlling transport of Cr were studied in the laboratory using fresh aquifer material and aquifer material that had been air-dried and stored under ambient conditions.

SITE CHARACTERISTICS

A detailed description of the hydrogeology of the CCTSHRS has been presented by LeBlanc (1984). Briefly, the aquifer is unconfined; the water table slopes to the south except where local effects of ponds perturb flow (fig. 1). The aquifer material consists of highly permeable, unconsolidated sand and gravel. Ground-water velocities range from 0.2 to 0.5 meter per day. Details of the procedures involved in performing and sampling the small-scale, natural gradient tracer tests are presented elsewhere (Davis,Kent, Rea, Maest, and Garabedian, 1991). At the oxic site, tracers were added to (oxic) recharge water and reinjected into the recharge zone (fig. 1). At the suboxic site, tracers were added

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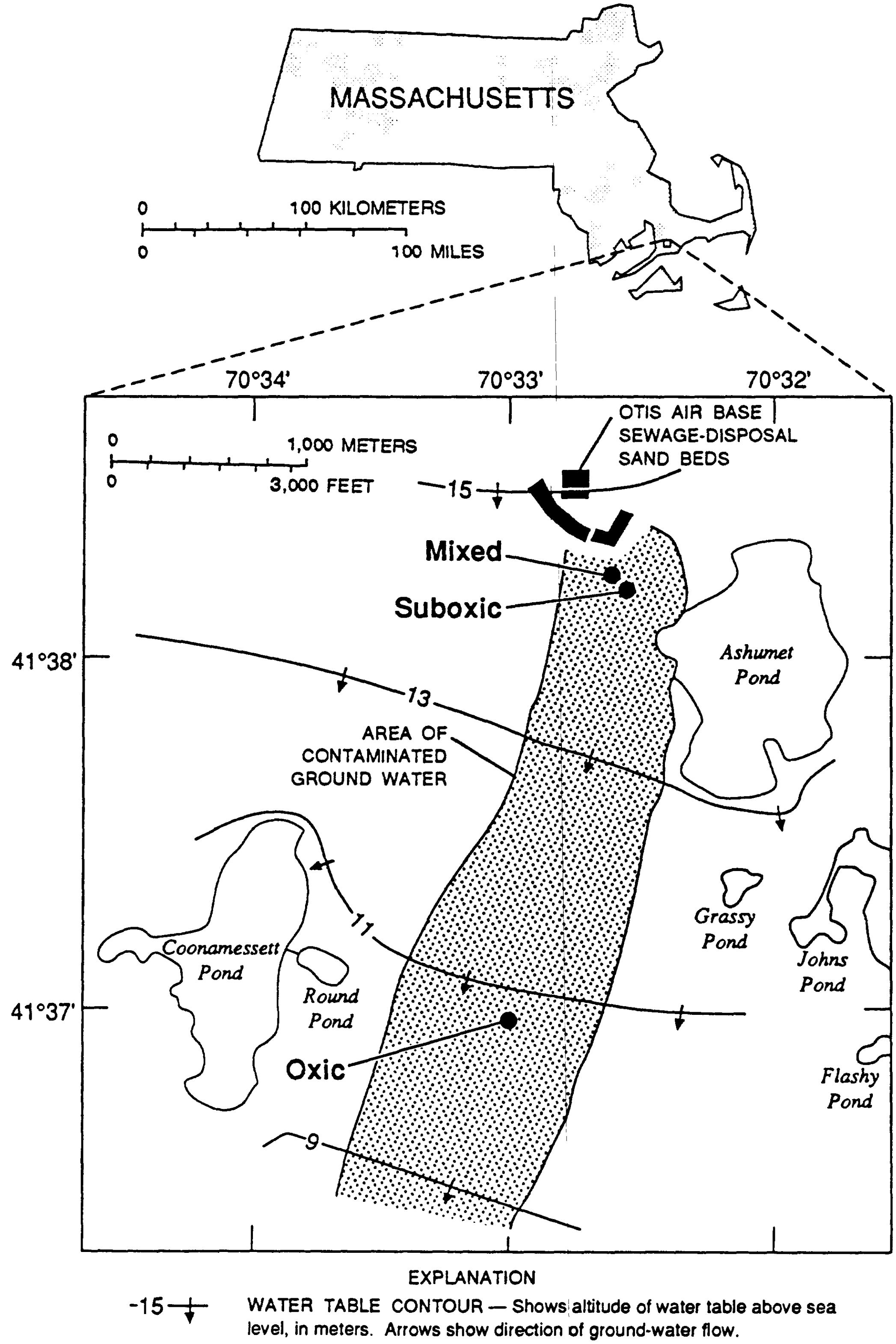
MASSACHUSETTS
0
100 KILOMETERS
0
100 MILES
70°34'
70°33'
70°32'
41°38'
41°37'
0
1,000 METERS
0
3,000 FEET
OTIS AIR BASE SEWAGE-DISPOSAL SAND BEDS
15
Mixed
Suboxic
13
AREA OF CONTAMINATED GROUND WATER
Ashumet Pond
11
Coonamessett Pond
Round Pond
Grassy Pond
Johns Pond
Flashy Pond
Oxic
9
EXPLANATION
-15
WATER TABLE CONTOUR — Shows altitude of water table above sea level, in meters. Arrows show direction of ground-water flow.

Figure 1. Location map showing the mixed, suboxic, and oxic natural-gradient tracer test sites. Dried, sieved subsurface material collected near the mixed suboxic site and near the oxic site. Fresh subsurface material was collected from the recharge zone near the mixed site.

to ground water from the sewage-contaminated (suboxic) zone and reinjected. At the mixed site, tracers were added to the ground water from the recharge zone and injected into the sewage-contaminated zone. The tracers were mixed into the ground water as dry powders. They included 1.9×10^{-3} M (molar) Br (added as KBr) and 1.0×10^{-4} M Cr(VI) (added as K_2CrO_4).

Tracer tests at the mixed and suboxic sites were performed using part of the array of multilevel sampling devices (MLS) (LeBlanc and others, 1991). At the mixed site, the tracer cloud was injected into three tubes (vertical separation of 0.25 m (meters)). Breakthrough curves were collected at various depths at MLS 4 and 22 m downgradient. At the suboxic site, the tracer cloud was injected into two tubes (vertical separation of 0.51 m). Breakthrough curves were collected at various depths 10 m downgradient from the injection.

The oxic site, located 2.3 kilometers downgradient from the other sites, includes a small cluster of MLS. The tracer cloud was injected into three tubes (vertical separation 0.38 m). There was a single MLS located 2 m downgradient from the injection at which breakthrough curves were collected at various depths.

Two sets of cores were collected for performing batch Cr removal experiments. Both sets were collected with a wireline, piston coring apparatus (Zapico and others, 1987). The first set included material from the recharge zone near the oxic site and material from the sewage-contaminated zone near the suboxic site. These cores were stored frozen, thawed prior to processing, dried at room temperature in a laminar-flow hood, dry-sieved through 2 millimeter nylon screen to remove gravel sized material, and stored in polyethylene bottles until used (12-16 months). The second set of cores were collected from the oxic zone near the mixed site. These cores were used in batch experiments that were initiated within a few hours of collecting the aquifer material. For these experiments, recharge water collected from the oxic zone near the mixed site was used.

LABORATORY METHODS

Experimental Setup

All experiments were conducted under oxic conditions in 40 milliliter polycarbonate centrifuge tubes (Nalgene). The pH was adjusted with 0.1 N HCl or NaOH.

Air-dried subsurface sands

Synthetic solutions with average field concentrations of the maor inorganic ions for recharge (pristine) waters and sewage-contaminated waters (table 1) were equilibrated with the air-dried sands for three consecutive washes. Washes were necessary to assure that major ion solution chemistry stabilized prior to the experiments to ensure reproducible results. Each wash was mixed overnight with an end-over-end tumbler prior to spiking with Cr(VI). Spiked experiments were mixed for 18 to 24 hours.

Desorption of Cr(VI) was accomplished by buffering the pH above 6 with NaH_2PO_4/NaOH, by adding sufficient sulfate (0.2 M) to effect desorption of Cr(VI), and mixing for 24 hours. This method was based on laboratory studies in the literature on Cr(VI) adsorption (Stollenwerk and Grove, 1985; Zachara and others, 1987; Eary and Rai, 1988) and was found to be effective in desorbing Cr(VI) in experiments where no reduction occurred (see below). The Cr removed by this reversible reaction is operationally defined as the adsorbed fraction. Thus, any chromium that was not desorbed was assumed to be reduced and is defined as such in this paper.

Table 1. *Major cation and anion concentrations of synthetic solutions*
[mM, millimolar]

	Sewage (mM)	Recharge (mM)
$CaSO_4$	0.25	0.025
$MgSO_4$	.15	.045
NaCl	1.3	.25
KCl	.10	----

Fresh subsurface sands

These experiments used oxic water collected from the recharge zone near the mixed site. Solution and sands were mixed for 1 to 24 hours. Desorption was accomplished in a similar manner to dried sands but the mixing time was decreased to 2 hours.

Chromium analysis

At the field site, Cr(VI) was analyzed by the diphenylcarbazide-spectrophotometric technique (Franson, 1985). Total Cr concentration was measured for field and laboratory water samples with an inductively coupled plasma apparatus using procedures recommended by the manufacturer. Chromium concentrations in samples analyzed by both methods were equal within analytical error, indicating that all of the dissolved Cr was present as Cr(VI).

RESULTS AND DISCUSSION

Chromium breakthrough curves from the tracer injection study at the oxic site show a loss of mass, suggesting reduction; and retardation, suggesting adsorption (fig. 2a). Adsorption onto mineral phases is indicated by the retardation of the Cr(VI) peak with respect to the nonreactive bromide peak (Davis, Kent, Rea, Maest, and Garabedian, 1991). The extensive tailing of the Cr(VI) peak probably results from slow desorption as ambient Cr(VI) concentrations decrease rather than reoxidation of Cr(III) (Stollenwerk and Grove, 1985, and see below). The integrated area under the Cr(VI) curve is estimated to be 60 percent of the area under the Br curve at a point 2 m from the point of injection. This decrease in Cr mass transport is probably due to reduction to Cr(III).

In contrast, Cr(VI) breakthrough curves from the mixed site showed no adsorption but suggested that reduction was significant (fig. 2b). Because the Cr(VI) peak was not

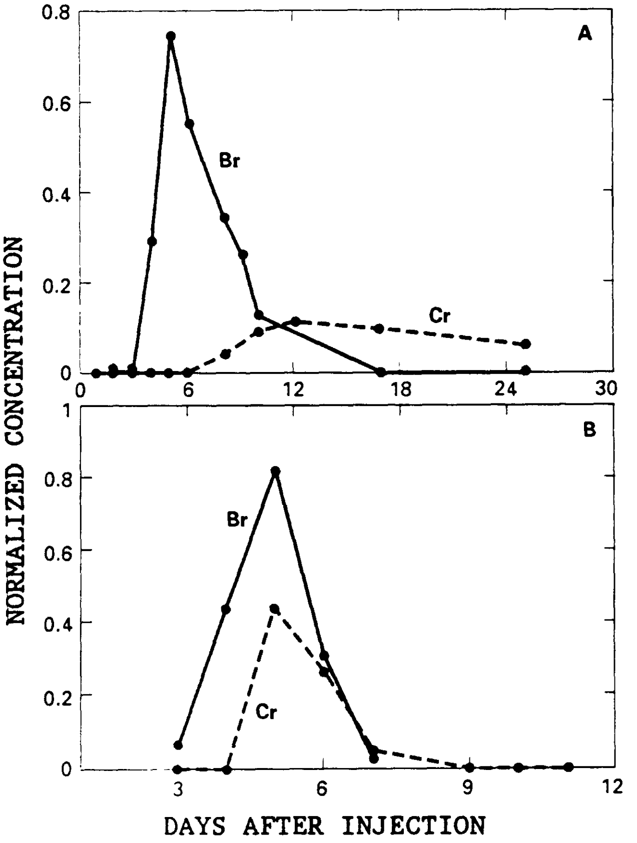

Figure 2. (A) Typical breakthrough curves for bromide and chromium in the recharge zone at the oxic site near the vertical center of the tracer cloud. The sampling point was 2 meters downgradient from the injection well at the oxic site. (B) Breakthrough curves for Br and Cr at the mixed site near the bottom of the tracer cloud, 4 meters downdgradient of the injection well.

retarded with respect to the bromide peak, no adsorption occurred, but the integrated area under the Cr(VI) curve was significantly smaller (48 percent of the area under the Br curve) than for bromide at a point 4 m downgradient and almost absent (6 percent of the area under the Br curve) by 22 m downgradient from the point of injection (data not shown). Attenuation of the peak area suggests that reduction is important. Cr transport at the suboxic site was similar to that observed at the mixed site.

Experiments with freshly collected aquifer material and oxic ground water gave results distinctly different from similar work with air-dried core material and synthetic recharge water. Thirty to 90 percent of the added Cr(VI) was removed in experiments with fresh sands, whereas 0 to 40 percent was removed in experiments with dried sands. After 24 hours of mixing, Cr(VI) removal by fresh sands from the oxic zone, in the presence of oxic water, was dominated by reduction whereas Cr(VI) removal in the presence of dried sands resulted predominantly from adsorption.

The fresh sands reduced 20 to 90 percent of the Cr(VI) added and the amount of reduction increased with time (fig. 3a). Cr(VI) reduction was greatest at low pH (fig. 3a, 4a), consistent with the results of kinetic studies (Eary and Rai, 1989). Reducing agents may include organic material or ferrous-containing minerals (Eary and Rai, 1989; Fish, 1991). The reduction of Cr(VI) by sands from the oxic zone appeared to be much slower than reduction rates of Cr(VI) in similar experiments with sands and ground water from the suboxic zone (Davis, Waite, Kent, and Anderson, 1991, this Proceedings). Note that there is no evidence for reoxidation of Cr(III) to Cr(VI) on the time scale of these experiments.

Adsorption of Cr(VI) onto fresh sands was the dominant mode of removal only in the presence of additional fine material and at low pH at the highest sand-to-solution ratios (2,000 g (grams) sand per liter solution) (fig. 4b). The presence of additional sorptive surfaces provided by extra fines and protonated mineral surfaces at low pH favored adsorption rather than reduction. This relation suggests that some of the minerals that adsorb Cr(VI) do not reduce it, and may successfully compete with the reducing agent when present in sufficient concentrations. However, Cr(VI) removal in kinetic experiments with sand-to-solution ratios of 400 g sand per liter (fig. 3a,b) changed from predominance of adsorption to predominance of reduction over a 24-hour period. Similar increases in reduction of Cr(VI) may occur with time even in the presence of additional sorptive surfaces.

Adsorption dominated the removal of Cr(VI) by dried sands from the oxic zone in the presence of synthetic and natural recharge water, although up to 20 percent was reduced (fig. 5a,b). On dried material from the suboxic zone, Cr(VI) reduction equaled Cr(VI) adsorption (fig. 5a,b) but was much less than reduction of Cr(VI) observed with fresh material (fig. 4a). The presence of natural water did not increase reduction with either the dried oxic or suboxic sand, suggesting that the dissolved organic compounds played an insignificant role in the process. Less-soluble organic material may be important in Cr(VI) reduction, but may be oxidized by the sand-drying and storage procedure. Also, there is evidence that oxygen can oxidize surficial ferrous iron in magnetite and ilmenite at pH 3 (White, 1990). Eary and Rai (1989) found that hematite and biotite maintain their ability to reduce Cr(VI) over a pH range of 3 to 10 after exposure to oxygen for 1 month. Further experiments are necessary to resolve the mechanisms of reduction in the oxic experiments.

The extent of adsorption on dried, sieved sands depended on the source of the material and the competing anion concentration in the synthetic or natural solutions (fig. 5b and 6b). Sands from the oxic site adsorbed up to 45 percent of the Cr(VI) from synthetic and natural recharge water at low pH values, and adsorption decreased to near-zero by pH 7 (fig. 5b and 6b). When the same material was mixed with synthetic sewage-contaminated water, Cr(VI) adsorption decreased at all pHs (fig. 5b). This observation is consistent with experiments by others that demonstrate the displacement of Cr(VI) from adsorption sites by a large excess of sulfate (Leckie and others, 1984; Zachara and others, 1987). Sands from the suboxic zone adsorbed very little Cr(VI) in synthetic sewage-contaminated water (fig. 5b). It is probable that low concentrations of potentially important adsorbents, such as iron and manganese oxides in the suboxic sands, in combination with sulfate concentrations in synthetic sewage-contaminated water (0.4 mM), limited Cr(VI) adsorption to less than 5 percent.

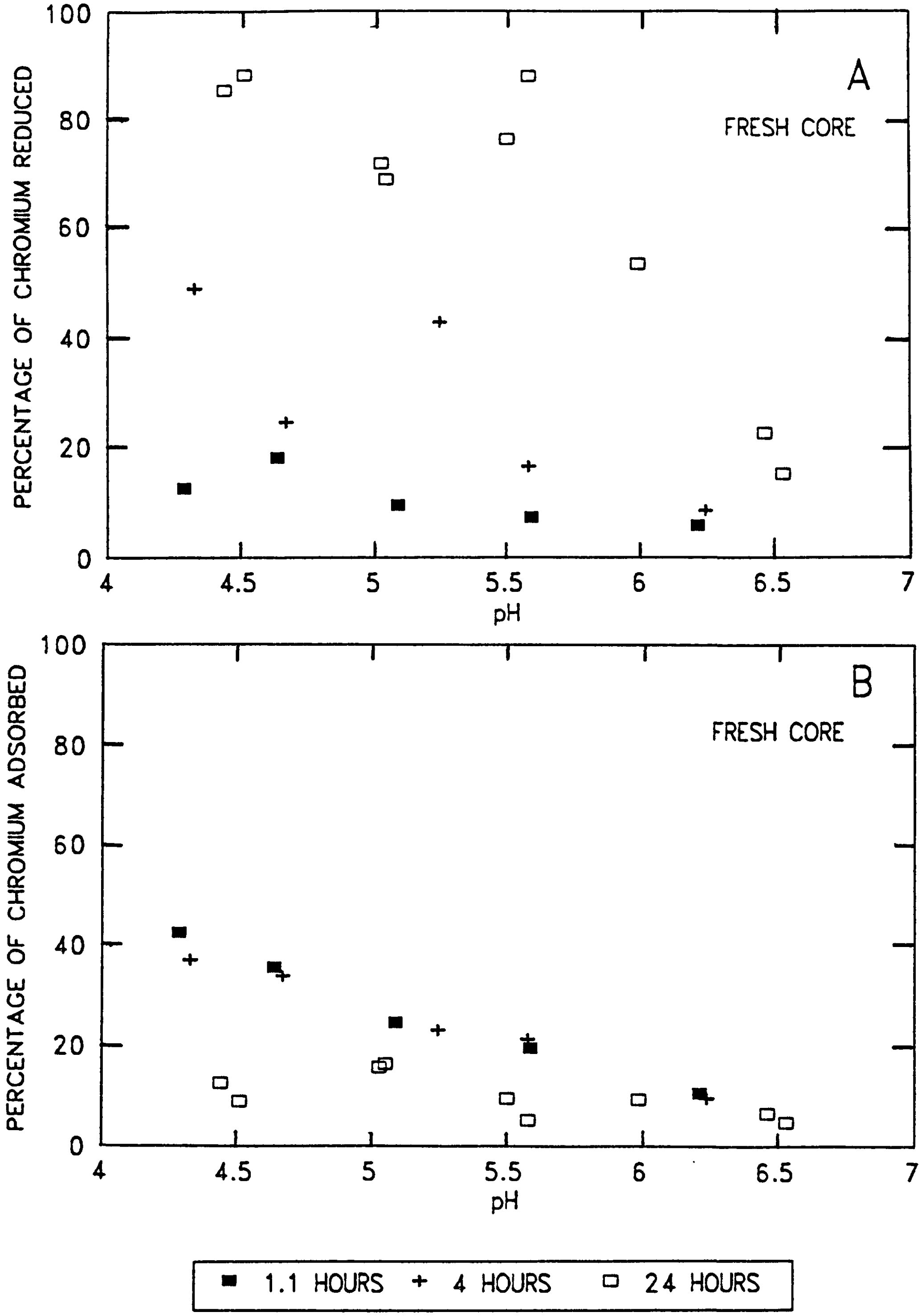

Figure 3. (A) Chromium (VI) reduction on fresh subsurface material from the oxic zone in oxic ground water as a function of pH and time. Solid/liquid ratio 400 grams per liter, initial concentration for Cr(VI) = 2 micromolar. (B) Cr(VI) adsorption on fresh subsurface material from the oxic zone in oxic ground water as a function of pH and time. Solid/liquid ratio 400 g/L, C_o= 2 micromolar.

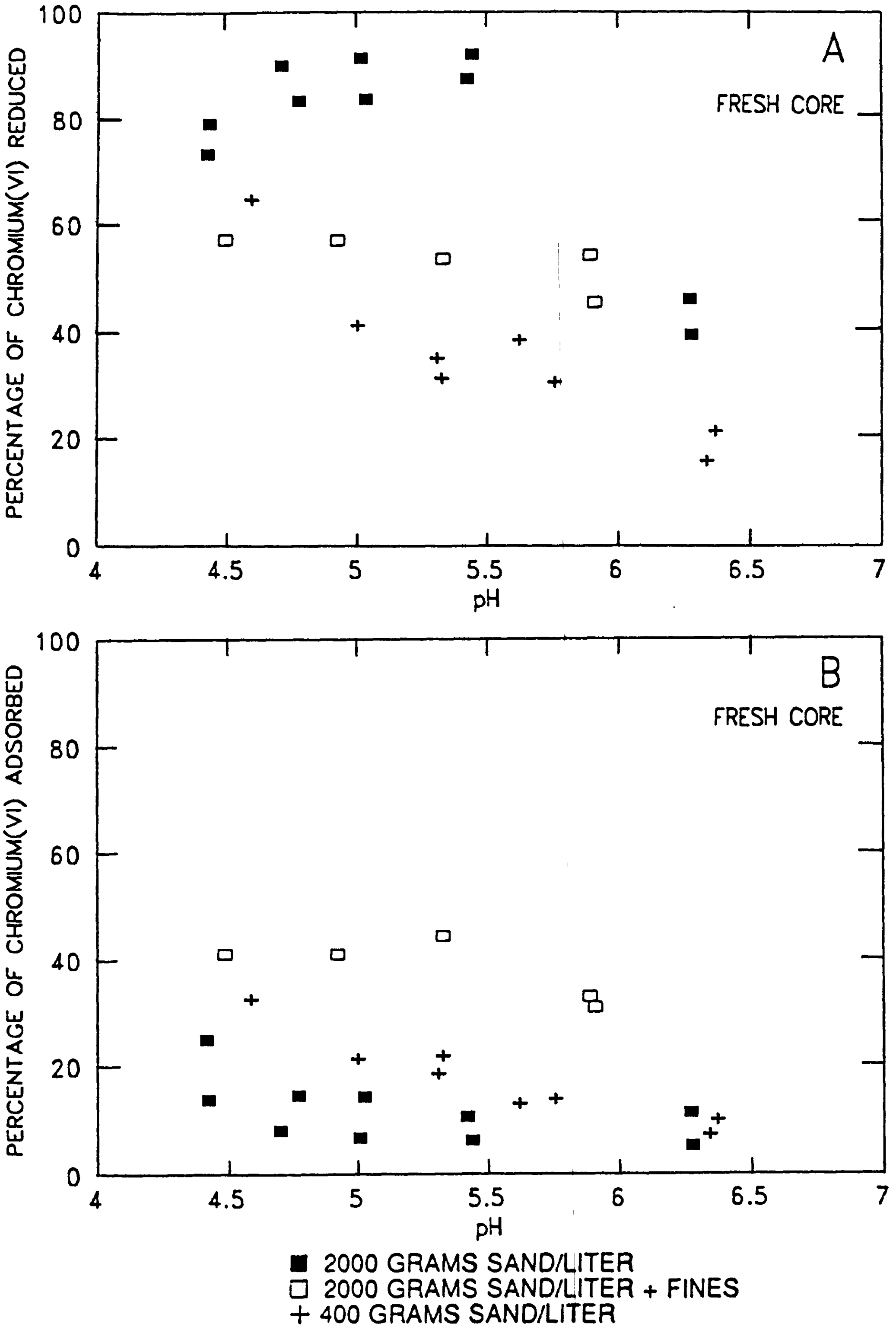

Figure 4. (A) Chromium(VI) reduction on fresh subsurface material from the oxic zone in oxic ground water as a function of pH and solid/liquid ratios. C_0= 8 micromolar. (B) Cr(VI) adsorption on fresh subsurface material from the oxic zone in oxic ground water as a function of pH and solid/liquid ratios. C_0=8 micromolar.

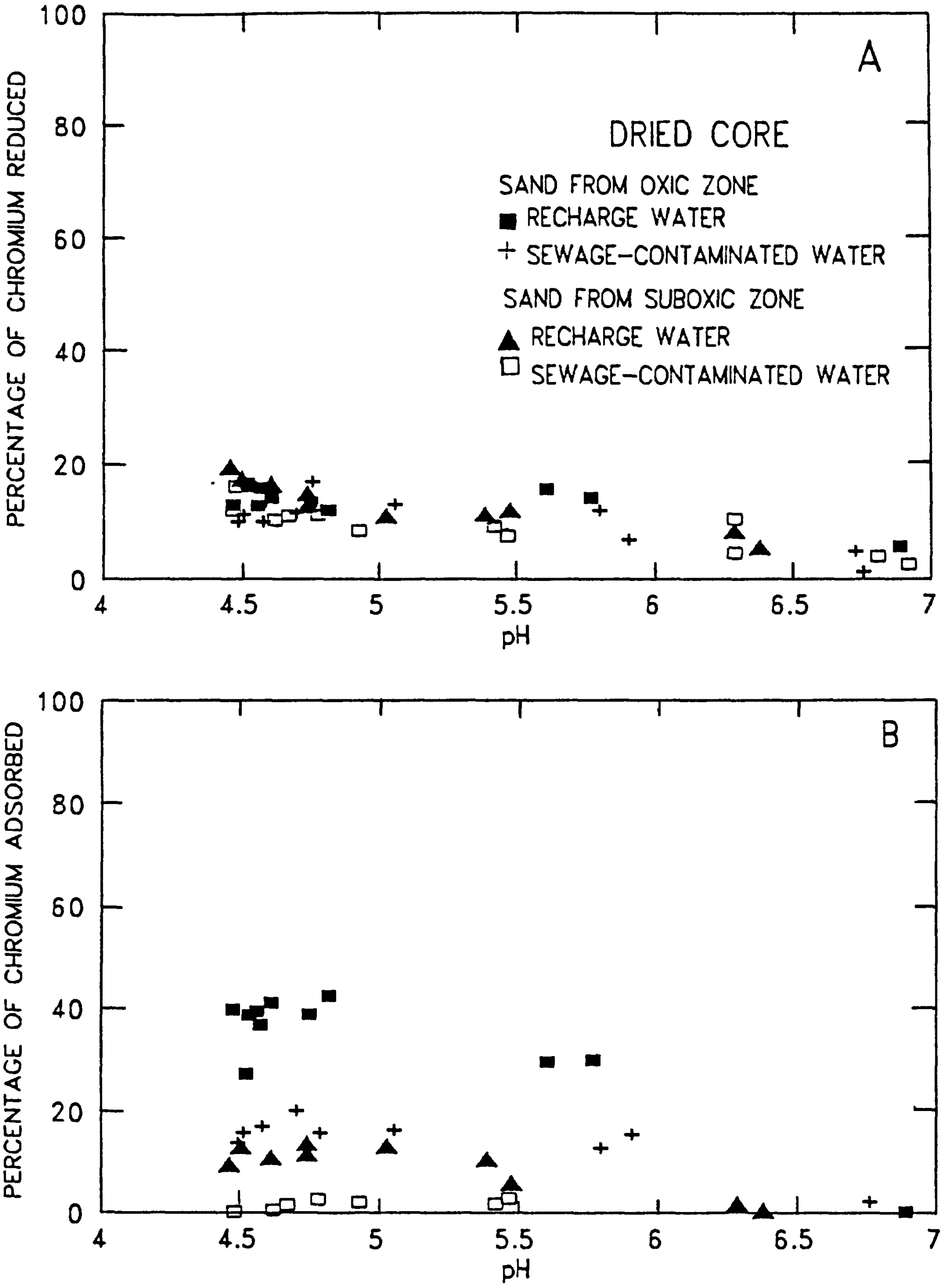

Figure 5. (A) Chromium(VI) reduction on dried subsurface material from the oxic and suboxic zones, in synthetic recharge and sewage-contaminated water. Solid/liquid ratio = 400 g/L, C_0 = 5 microliters. (B) Cr(VI) adsorption on dried subsurface material from the oxic and suboxic zones in synthetic recharge and sewage-contaminated water. Solid/liquid ratio = 400 g/L, C_0 = 5 micromolar.

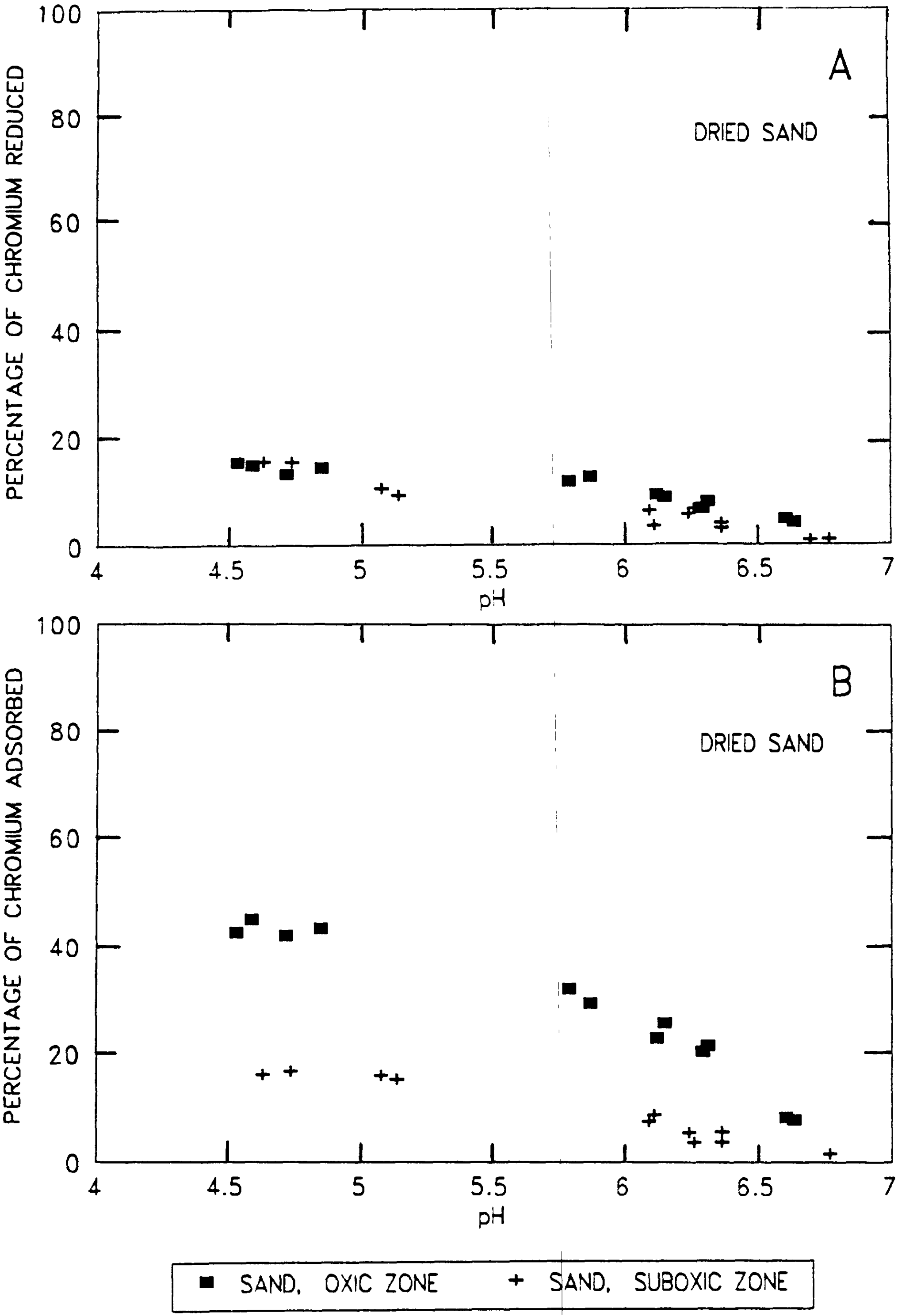

Figure 6. (A) Chromium(VI) reduction on dried subsurface material from the oxic and suboxic zones in natural waters from the recharge zone. Solid/liquid ratio = 400 g/L, C_0 = 5 microliters. (B) Cr(VI) adsorption on dried subsurface material from the oxic and suboxic zones in natural water from the recharge zone. Solid/liquid ratio = 400 g/L, C_0 = 5 micromolar.

SUMMARY

Result of tracer injection studies indicate that reduction and adsorption of Cr(VI) occurred in oxic recharge zone, but only reduction occurred in suboxic sewage-contaminated zone. Freshly collected core material and water from the recharge zone substantiated reduction by the oxic sands. Reductive potential is diminished in air-dried sands from both the oxic and suboxic zones, probably as a result of oxidation of sorbed organic material or surfaces of ferrous-containing minerals. Reduction by dried sands was independent of the water composition and whether sand was collected from the oxic or suboxic zone.

Adsorption decreased and reduction increased with fresh subsurface material. Adsorption on fresh core material for experiments lasting 24 hours was generally less than 20 percent except in the experiment with extra fines. Thus, experiments on fresh subsurface material suggest that adsorption only successfully competes with reaction when additional sorptive surfaces are available, and that with longer time periods, adsorption may play an insignificant role.

Adsorption on dried sands from both the oxic and suboxic zones was dependent on solution pH and competing anion concentration. However, adsorption decreased significantly on sands from the suboxic zone as compared to the oxic zone. This difference probably is a result of compositional differences.

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REDUCTION AND TRANSPORT OF CHROMIUM(VI) UNDER MILDLY REDUCING CONDITIONS IN A SAND AND GRAVEL AQUIFER, CAPE COD, MASSACHUSETTS

By J.A. Davis[1], T.D. Waite[2], D.B. Kent[1] *and* L.D. Anderson[1]

ABSTRACT

Field tracer tests and laboratory experiments with freshly collected glaciofluvial sediments have demonstrated that reduction of chromium (Cr)(VI) is a significant process controlling the mobility of Cr in the sewage-contaminated zone of the aquifer at the Cape Cod Toxic-Substances Hydrology Research Site. Removal of Cr(VI) from ground water in this suboxic zone occurred only by reduction to Cr(III), which was strongly and irreversibly sorbed. The effect of the chemical reactions on Cr(VI) transport is an attenuation of Cr mass transport relative to that of a nonreactive tracer. Interestingly, the attenuation is not accompanied by retardation in Cr transport. This occurs because all Cr(III) is rapidly and irreversibly sorbed, and Cr(VI) adsorption is negligible under the conditions present in the sewage-contaminated zone. The reduction process is highly pH-dependent, and the likely reductants are particulate organic carbon or the surfaces of ferrous-containing minerals, such as biotite and magnetite.

INTRODUCTION

Chromium (Cr)(VI) is an anionic contaminant present in various industrial and power generation wastes that are often disposed onto the land surface. In domestic waters, Cr(VI) is a regulated constituent (U.S. Environmental Protection Agency, 1986) because it can be toxic to humans and other organisms. Adequate protection of subsurface water supplies requires that fundamental properties of Cr(VI) reactions with subsurface materials be known. An important modeling question is whether the transport of redox-sensitive elements such as Cr can be better predicted with an equilibrium or reaction rate-based modeling approach (Lindberg and Runnells, 1984; Fish, 1991).

Tracer-injection tests have been performed in a shallow, sand and gravel aquifer at the U.S. Geological Survey Cape Cod Toxic-Substances Hydrology Research Site (CCTSHRS) near Falmouth, Mass. (fig. 1). The permeable, granular aquifer is typical of many glaciofluvial aquifers in the northeastern part of the United States that are particularly susceptible to anthropogenic contamination (Hess, 1989). The tracer tests have been conducted within the oxic recharge zone and suboxic sewage-contaminated zones of the aquifer (Davis, Kent, Rea, Garabedian, and Anderson, 1991, this Proceedings). The results have shown that aquifer chemistry strongly affects the transport of Cr(VI) in the aquifer (Davis, Kent, Rea, Maest, and Garabedian,1991).

Cr(VI) reduction can occur by chemical or biological processes (Davis, Kent, Rea, Garabedian, and Anderson, 1991, this Proceedings). To improve understanding of the mechanisms of Cr reduction in the aquifer and the variables that influence the rate of the process, a detailed set of experiments was performed in November 1990, using subsurface material and ground water from the suboxic sewage-contaminated zone of the aquifer at CCTSHRS. In this paper we present the results of these experiments and discuss their significance in the context of modeling the transport of Cr(VI) in ground water. Transport of Cr(VI) in the oxic recharge zone is discussed by Anderson and others, 1991 (this Proceedings).

MATERIALS AND METHODS

Kinetic batch experiments were conducted with freshly collected subsurface material and ground water from the suboxic, sewage-contaminated zone of the shallow aquifer at CCTSHRS (near the mixed site shown in figure 1; see Davis, Kent, Rea, Garabedian, and Anderson, 1991, this Proceedings), for a discussion of aquifer chemistry and tracer test sites). The median grain size of the sediments is 0.6 millimeters, and it generally contains less than 1 percent silt and clay by weight. Quartz, plagioclase, and orthoclase comprise 90 percent by weight of the minerals; the remaining 10 percent consists of biotite, hornblende, muscovite, and other accessory minerals (Barber, 1987). Procedures for collecting and analyzing ground-water samples are presented in Davis, Kent, Rea, Maest, and Garabedian (1991). Because of the requirement of working with fresh material (to prevent oxidation), experiments were conducted with four different cores collected over a 2-week interval. All cores were collected using a modified wire-line piston corer in 1.5 m (meter) sections (Zapico and others, 1987) without the introduction of water to clear the core barrel during coring. Suboxic ground-water was collected from the same elevations as subsurface material, using a multilevel sampling device (MLS) located about 10 m from the coring location.

Batch experiments were begun within 3 hours after core collection. Subsurface material from a 0.6 m length of core was removed from the core liner and homogenized in a glove bag purged with nitrogen gas. An aliquot of the wet sand was then placed in a polycarbonate centrifuge tube and mixed with suboxic ground water. Wet sand and water weights were recorded to allow quantification of the water mass in each experiment after determination of the dry sand-weights. Cr(VI) was then added from a concentrated stock solution to achieve the desired initial concentration. The tubes were placed on an end-over-end rotator in a temperature-controlled environment. Dissolved Cr(VI) concentrations were determined after various reaction times on filtered samples (0.45-micrometer membrane filter) by measuring the absorbance of the Cr(VI) complex formed

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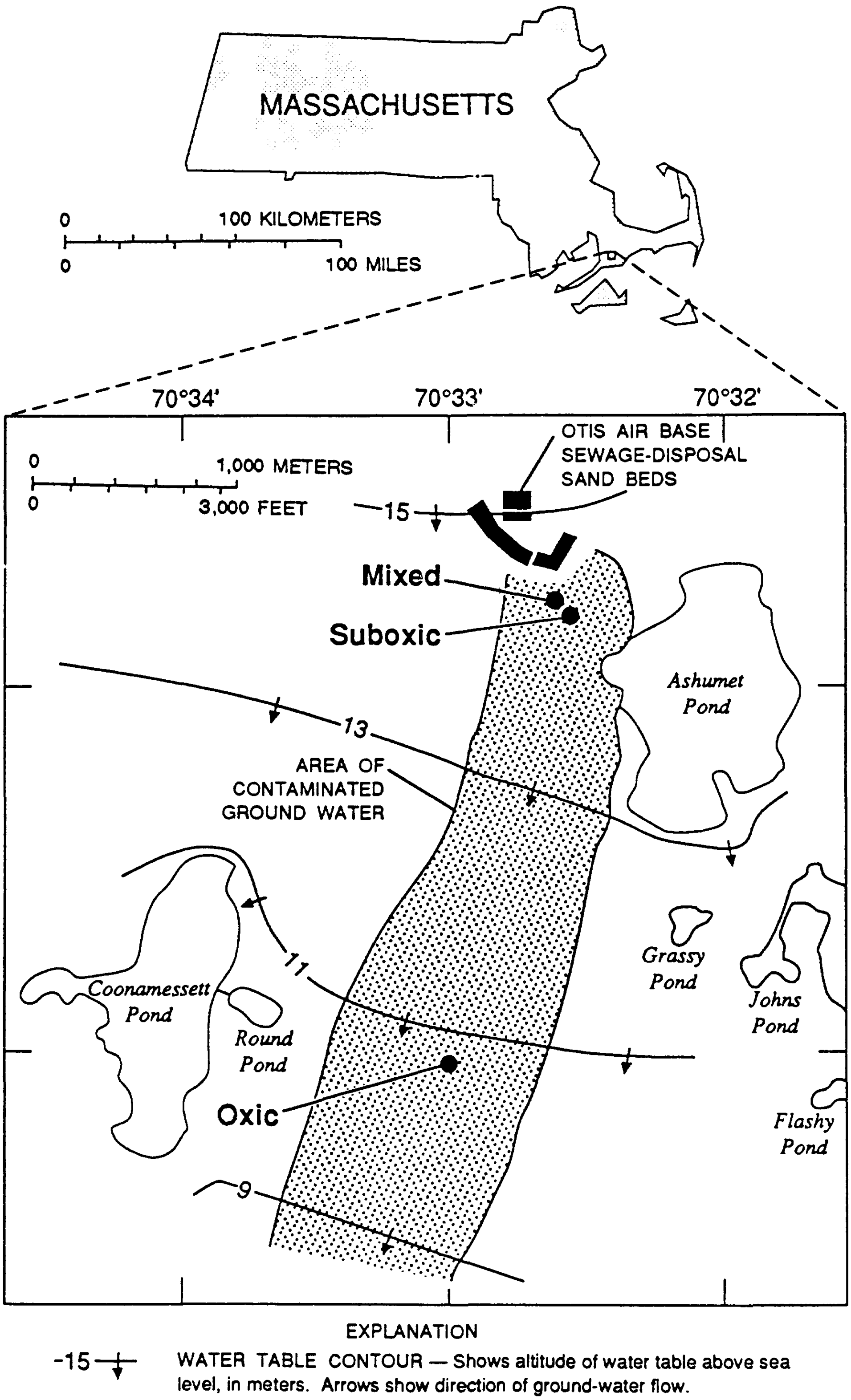
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Ashumet
Pond
13
AREA OF
CONTAMINATED
GROUND WATER
11
Grassy
Pond
Coonamessett
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Round
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Johns
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Oxic
Flashy
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EXPLANATION
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WATER TABLE CONTOUR — Shows altitude of water table above sea level, in meters. Arrows show direction of ground-water flow.

Figure 1. Map showing the locations of tracer-injection test sites at the Cape Cod Toxic-Substances Hydrology Research site near Falmouth, Massachusetts. Subsurface material and ground water were collected near the mixed site for laboratory experiments on the rate of chromium(VI) reduction.

with diphenylcarbazide. Preliminary results demonstrated that the polycarbonate tubes did not allow an invasion of oxygen (<100 parts per billion) over the course of the kinetic experiments. In addition, it was found that Cr(VI) reduction rates were identical for tubes rotated inside and outside of the glove bag. The methods used for desorption measurements are given in Anderson and others (1991, this Proceedings).

RESULTS AND DISCUSSION

Batch Experiments

Desorption experiments were conducted throughout the kinetic batch experiments; the results (not presented here) showed that reversible Cr(VI) adsorption was negligible under the conditions present in the sewage-contaminated water. This result is consistent with the fact that Cr(VI) is weakly adsorbed by iron oxides only under conditions of low pH and low concentrations of competing anions (Zachara and others 1987; Davis and Kent, 1990). Batch experiments with air-dried sand from the sewage-contaminated zone of the aquifer demonstrate that Cr(VI) adsorption is inhibited by the relatively high concentrations of sulfate present in ground water in this zone (Anderson and others, 1991, this Proceedings). Thus, all Cr(VI) removal from solution in the batch experiments discussed here can be attributed to reduction to Cr(III), which is strongly and irreversibly sorbed by sediments (Sass and Rai, 1987; Schultz and others, 1987), as long as it remains uncomplexed with organic ligands. The results of tracer tests (discussed below) in the suboxic zone support the conclusion that all Cr(VI) reduced was sorbed; no dissolved Cr(III) was detected during these tests despite significant reduction of Cr(VI).

Batch experiments with sand and ground water from the suboxic zone were conducted in two ways: (1) using centrifuge tubes that were opened only once for immediate sampling (single-point), and (2) using tubes that were sampled repeatedly over time (sequential), which allowed the headspace of the tube to fill with air after the first sampling. The rate of Cr(VI) reduction was similar for each method; a slight difference in the rate of reduction was observed after 36 hours of reaction (or 24 hours after the first exposure to air in the sequential tubes). The rate of Cr(VI) reduction was decreased substantially in the presence of aerated ground water (using the same ground water, except that 6 parts per million dissolved oxygen was introduced by bubbling air). No reduction was observed in the presence of suboxic ground water alone.

The rate of Cr reduction as a function of temperature is illustrated in figure 2. Under most conditions, Cr reduction could be characterized by processes occurring in two time regimes: (1) a fast process that reached completion in less than 30 minutes, and (2) a slower process that continued for longer than 60 hours. Increasing the temperature appeared to have little effect on the extent of initial reduction, but significantly increased the rate of the slower process (fig. 2). The dependence of the rate of the slow process on temperature suggests that a diffusion-limited process controls the rate, for example, intragranular diffusion (Wood and others, 1990), but confirmation of this hypothesis will require further research.

Investigations of microbial reduction of Cr(VI) (Komori and others, 1989; Wang and others, 1989) have reported a maximum rate in the range of 30 to 40 °C (degrees Celsius). In contrast, no temperature optimum was observed in these experiments; instead, the reduction rate increased monotonically with increasing temperature. These results suggest that the primary mechanism of Cr(VI) reduction was abiotic. This hypothesis was supported by the results of an experiment with microwave-sterilized sand/water mixtures, using the method of Keller and others (1988). The microwave treatment was followed by addition of Cr(VI), and it was observed that the rate of Cr(VI) reduction was not affected by the sterilization procedure.

Of all variables investigated, pH was the most important in affecting the rate of Cr reduction (fig. 3). At pH 4.6, Cr reduction was virtually complete within 30 minutes at an initial Cr(VI) concentration of 10 mM (micromolar) (0.52 milligrams per liter) and a sand-water ratio of 900 grams per liter. Decreasing the pH had a dramatic effect on the amount of Cr reduced initially, but appeared to have little effect on the rate of the slower process (fig. 3).

The most likely reductants associated with the solid phases are particulate or sorbed organic compounds and Fe(II)-containing minerals in the sand, for example, biotite and magnetite (White, 1990; Eary and Rai, 1989). Although no reduction of Cr(VI) was observed with suboxic water alone at the *in-situ* pH and at 20 °C, the effect of pH and temperature changes on reduction of Cr(VI) by dissolved solutes was not examined. Such changes could have affected the concentration of dissolved Fe(II), which is known to reduce Cr(VI) rapidly (Eary and Rai, 1988). Changes in the concentration of dissolved Fe(II) before the addition of Cr(VI) conceivably could have affected the extent of Cr(VI) reduction occurring in the fast process (figs. 2 and 3).

Estimating the order of the reduction process with respect to Cr(VI), H^+, and concentration of reductant is complicated by the likelihood of multiple parallel oxidation-reduction reactions and the separation of fast and slow processes in the early stage of the process. Parallel reactions could be caused by the participation of two or more reductants, each with its own rate law. The order with respect to Cr(VI) concentration during the first hour of reaction was estimated by plotting the slope of the initial reaction trajectory (based on a least-squares linear slope from time zero) against the initial Cr(VI) concentration (fig. 4). The rate was virtually zero order at low Cr(VI) concentrations, but shifted to a higher order at the highest Cr(VI) concentration investigated. However, if the initial reduction of Cr(VI) by the sand is subtracted before the rate of further reduction is estimated, significantly different results are obtained. The assumption of a constant rate of Cr(VI) reduction during the first hour of the process is probably a poor one.

The reductive capacity of the sand was estimated from 100-hour batch experiments with excess Cr(VI) at 55 °C. These results suggested that the sand was capable of reducing more than 50 nanomoles of Cr(VI) per gram of sand, which is equivalent to 200 micromoles of Cr(VI) per liter of ground water at the porosity of 0.4 in the aquifer.

Field Tracer Tests

Three tracer-injection tests were performed in July 1988, in which several hundred liters of ground water containing 100 µM Cr(VI) were injected into the suboxic zone of the aquifer. Details of the tracer tests are given in Davis, Kent, Rea, Maest, and Garabedian (1991) and Davis, Kent, Rea, Garabedian, and Anderson (1991, this Proceedings). Typical breakthrough curves for dissolved Cr and bromide (Br, a nonreactive tracer) injected into the sewage-contaminated zone are shown in Figure 5B, for a sampling point 4 m downgradient from the injection point (the mixed site in fig. 1). The peak in dimensionless Cr concentration was considerably attenuated relative to the peak of the nonreactive tracer, bromide (Br), suggesting a loss of Cr mass being transported in the ground water. Virtually all dissolved Cr had been removed from the ground water after the tracer cloud had traveled 22 m downgradient. However, despite the attenuation of Cr mass transport, the peaks in Cr and Br dimensionless concentrations occurred at nearly the same time (fig. 5B), indicating negligible retardation. This type of transport can be contrasted with the results observed in the recharge zone (fig. 5A), in which Cr transport was both attenuated and retarded. Subsequent tracer tests conducted in 1989 have shown that all dissolved Cr in the ground water in either the recharge zone or the sewage-contaminated zone is present as Cr(VI); that is, no dissolved Cr(III) was detected.

The results of the tracer-injection studies in the suboxic zone of the aquifer and the batch studies discussed above are consistent. The reduction of Cr(VI) to Cr(III) should cause a decrease in the mass of Cr being transported as the tracer cloud moves downgradient, because inorganic Cr(III) species are rapidly and irreversibly sorbed. This is observed in the field experiments as an attenuation of the peak dimensionless Cr concentration relative to that of Br (fig. 5B). The rate of the reduction processes coupled with the rate of ground water flow will determine the distance that Cr(VI) is transported downgradient. In addition, the fact that Cr(VI) adsorption by the sands was negligible under the conditions found in the suboxic zone is consistent with the lack of retardation of the Cr peak observed in the tracer test in that zone (fig. 5B). In contrast, under the conditions found in the recharge zone, Cr(VI) adsorption is significant (Anderson and others, 1991, this Proceedings) and retardation of Cr (VI) transport relative to that of Br is observed (fig. 5A). In addition, some attenuation of the Cr mass transport is indicated, and this is supported by observations of Cr(VI) reduction by the sands found in the recharge zone (Anderson and others, 1991, this Proceedings).

CONCLUDING REMARKS

One of the important implications of this research is that Cr(VI) mobility in the aquifer may be more accurately predicted by a model formulated from semiempirical observations of reaction kinetics rather than equilibrium calculations based on redox potentials. In the reaction rate modeling approach, the important reactions of Cr(VI) in the environment need to be assessed, the environmental variables that control the reaction rate need to be identified, and the rates and stoichiometries of the reactions should be measured under the conditions expected in the environment. We have shown here that Cr(VI) reduction is the most important process to be considered. The rate of Cr reduction was highly dependent on pH and the concentration of reductants, and was somewhat dependent on the concentration of Cr(VI) in the ground water. However, the identity of the reductants and the stoichiometry of the reactions remain unknown. Future research on this project will

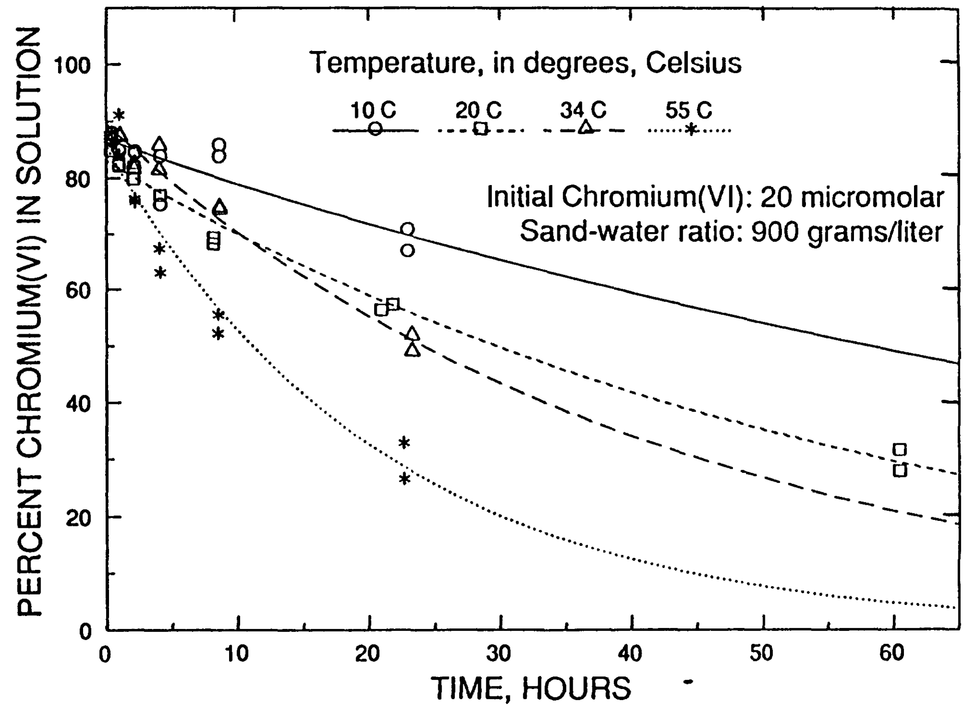
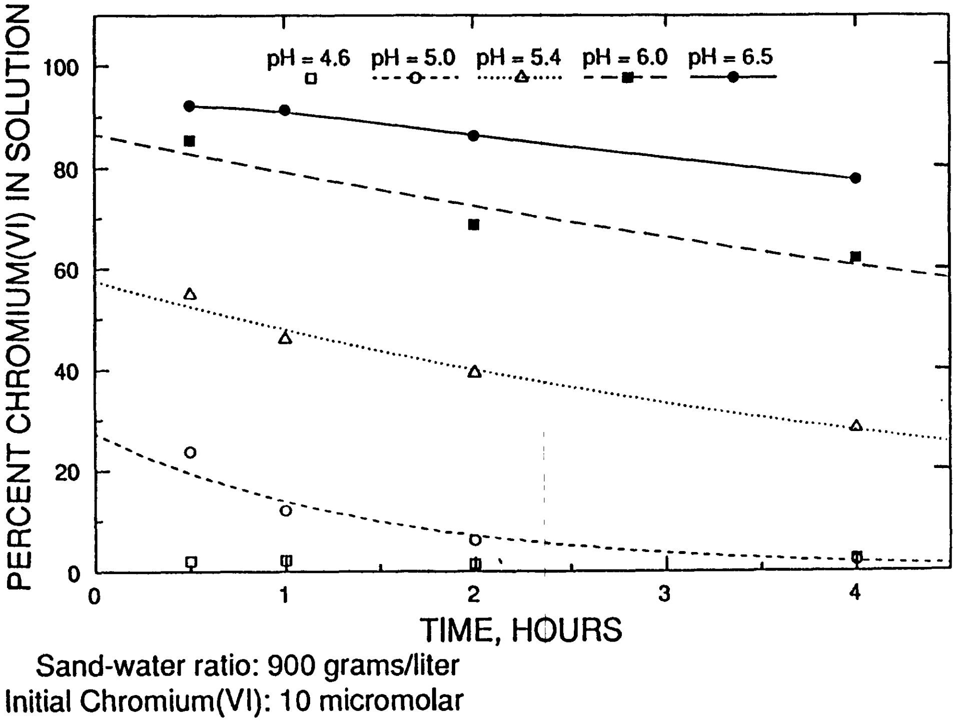


Figure 2. Temperature dependence of chromium(VI) reduction in batch experiments with freshly-collected subsurface material and suboxic ground water. pH of the water in all experiments was 6.5 +/- 0.1.



Sand-water ratio: 900 grams/liter
Initial Chromium(VI): 10 micromolar

Figure 3. pH dependence of chromium(VI) reduction in batch experiments with subsurface material in sand-ground water mixtures adjusted to different initial pH values before chromium(VI) addition.

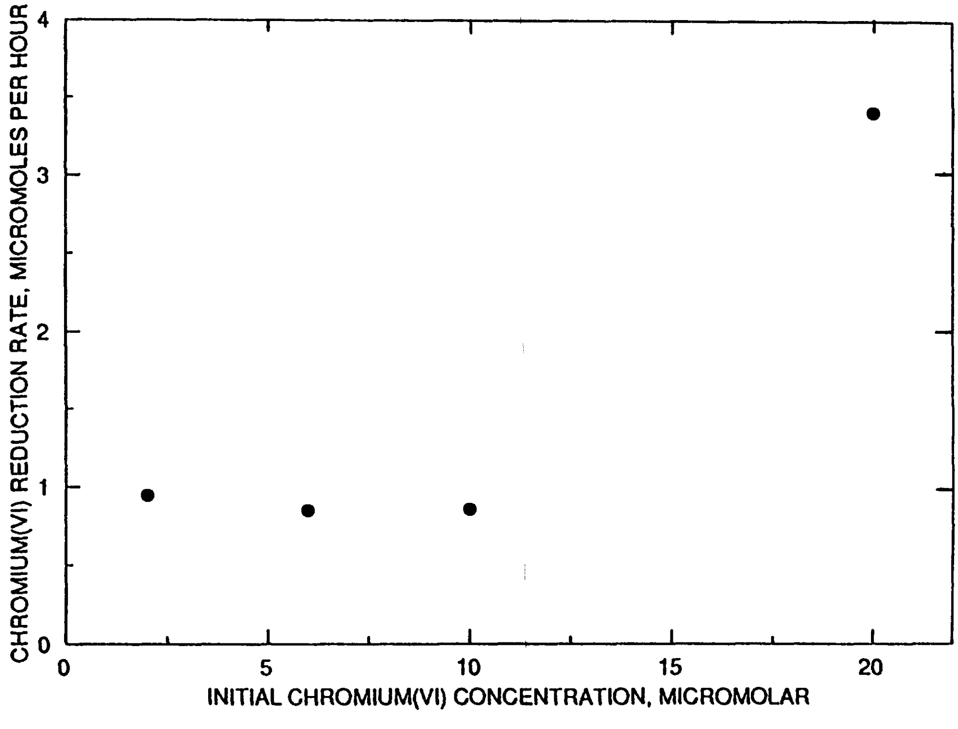


Figure 4. Rate of chromium(VI) reduction in batch experiments with subsurface material and ground water as a function of the initial chromium(VI) concentration. pH of the water was 6.5.

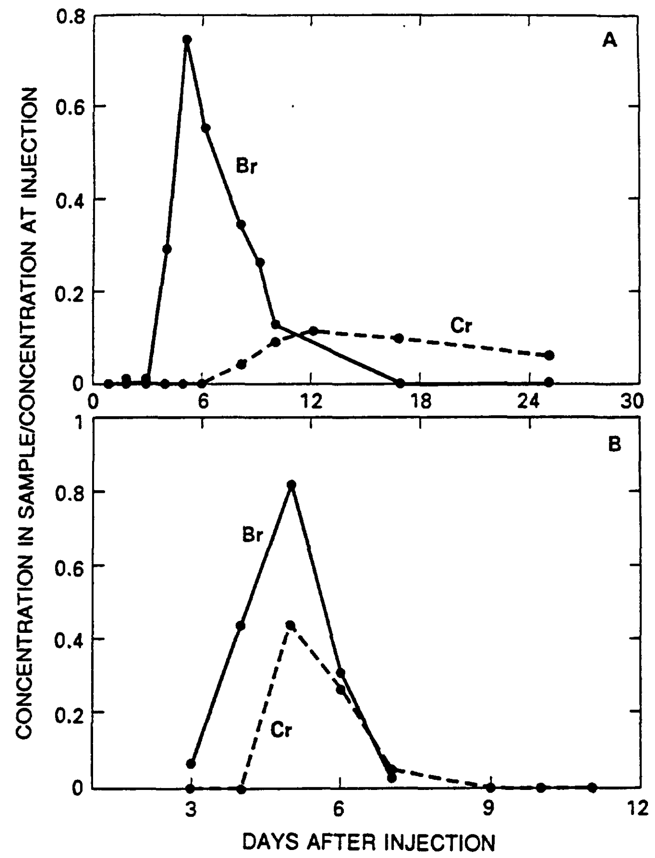


Figure 5. (A). Breakthrough curves for chromium and bromide in the oxic, recharge zone at the oxic site (see fig. 1). The sampling point was 2 meters downgradient from the injection well. (B). Breakthrough curves for chromium and bromide in the suboxic, sewage-contaminated zone at the mixed site (see fig. 1). The sampling point was 4 meters downgradient of the injection well.

include a comparison of Cr transport predicted from a coupled flow-reaction model to that observed in the tracer tests. In addition, one may compare the rate of Cr reduction calculated from simulating the tracer test data to the rates observed in the batch experiments. Before an accurate modeling effort can be applied, however, more information will be needed about the abundance and type of reductants in the aquifer and their spatial variablity.

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TRANSPORT OF ZINC IN THE PRESENCE OF A STRONG COMPLEXING AGENT IN A SHALLOW AQUIFER ON CAPE COD, MASSACHUSETTS

By D.B. Kent[1], J.A. Davis[1], L.D. Anderson[1], *and* B.A. Rea[1]

ABSTRACT

Small-scale natural-gradient tracer tests were performed in pristine and sewage-contaminated zones of a shallow, sand and gravel aquifer on Cape Cod, Massachusetts. Transport of tracers, including zinc (Zn), ethylenediaminetetracetic acid (EDTA), and bromide (Br), (the unreactive tracer) was determined in each zone. In the sewage-contaminated zone, where the pH was near 6.0 and dissolved salt concentrations were moderately high, Zn was transported conservatively as Zn-EDTA complexes. In the pristine recharge zone, where the pH was near 5.0 and concentrations of dissolved salts were low, Zn was greatly retarded. Retardation was probably caused by displacement of Zn from EDTA complexes by Fe(III) leached from aquifer material and extensive adsorption of the Zn^{2+} *ion, although adsorption of Zn-EDTA complexes could not be ruled out. Additional tracer tests have been performed to examine Zn and EDTA speciation; these results will aid in determining the predominant adsorption mechanisms. The results illustrate the importance of speciation and adsorption properties in controlling transport and how aquifer chemistry affects speciation and transport.*

INTRODUCTION

Adsorption and complexation reactions affect the transport of hydrolyzable metal ions (Davis and others, 1991). In noncomplexing solutions, cationic metals exist as free metal ions and hydrolysis species, which are strongly adsorbing species. The presence of dissolved ligands, such as ethylenediaminetetracetic acid (EDTA), can greatly enhance the mobility of metal ions by forming weakly adsorbing complexes (Means and others, 1978; Davis and others, 1991; Rea and others, 1991, this Proceedings). In this paper, we present initial results of ongoing research on the competing roles of adsorption and complexation reactions in the transport of metal ions in ground water.

The effect of adsorption and complexation on transport has been investigated by performing small-scale, natural-gradient tracer tests. The experiments involved injecting ground water, to which dissolved zinc (Zn) and EDTA had been added, into chemically distinct zones of a shallow, sand and gravel aquifer. Breakthrough of the tracers was monitored at various sampling points downgradient from the injection well. The dominant Zn-EDTA complexes under the conditions of the experiments, $ZnEDTA^{2-}$ and $ZnHEDTA^{-}$, are weakly adsorbing species (Davis and others, 1991). Zn^{2+}, which is the dominant Zn species in the absence of EDTA at the ambient ground-water pH values, is a strongly adsorbing, greatly retarded species (Rea and others, 1991, this Proceedings).

FIELD-SITE DESCRIPTION

Small-scale natural-gradient tracer tests were performed at the U.S. Geological Survey Cape Cod Toxic-Substances Hydrology Research Site (CCTSHRS, fig. 1). The hydrogeology of the CCTSHRS is described in LeBlanc (1984). As shown in figure 1, the aquifer is unconfined; the water table slopes to the south except where perturbed by ponds. The aquifer material consists of highly permeable, unconsolidated sand and gravel. Ground water velocities range from 0.2 to 0.5 meters per day.

An extensive plume of sewage-contaminated ground water (also referred to as the sewage plume) has resulted from disposal of effluent from the Otis Air Base sewage-treatment facility onto rapid infiltration beds. The infiltration beds and sewage plume are illustrated in figure 1.

The presence of the sewage plume gives rise to a vertical gradient in ground-water chemistry. A recharge zone, derived from precipitation, overlies the sewage plume. Chemical characteristics of the recharge and sewage-contaminated zones are summarized in table 1. Redox conditions in the sewage-contaminated zone are characterized by denitrification and manganese (Mn) reduction; conditions are not sufficiently reducing to yield appreciable concentrations of ferrous (Fe(II)) or dissolved sulfide (Davis and others, 1991). The recharge zone becomes thicker with increasing distance downgradient from the disposal beds (that is, to the south).

Detailed studies of the mineralogy of the aquifer material are underway; only the general characteristics are presented here. Quartz, plagioclase, and orthoclase constitute greater than 90 percent by weight of the minerals; biotite, hornblende, muscovite and other accessory minerals comprise the remainder (Barber, 1987). Organic material and clay minerals constitute less than 0.1 percent by weight (Barber, 1987). Chemical extractions were performed to assess the quantities of poorly crystalline ferric (Fe(III)) and Mn hydrous oxides (Davis and others, 1991). Fe and Mn concentrations in the aquifer material were about 2 and 0.1 micromoles per gram, respectively.

METHODS

Tracer tests exploited the differences in chemistry between the recharge and sewage-contaminated zones (fig. 2). At site O, (labeled "Oxic" in fig. 1), tracers were added to recharge water and reinjected into the recharge zone. At site S (labeled "Suboxic" in fig. 1), tracers were added to ground water from the sewage-contaminated zone, which was suboxic, and reinjected. At site M (labeled "Mixed" in fig. 1), tracers were added to ground water from the recharge zone and injected into the sewage-contaminated zone.

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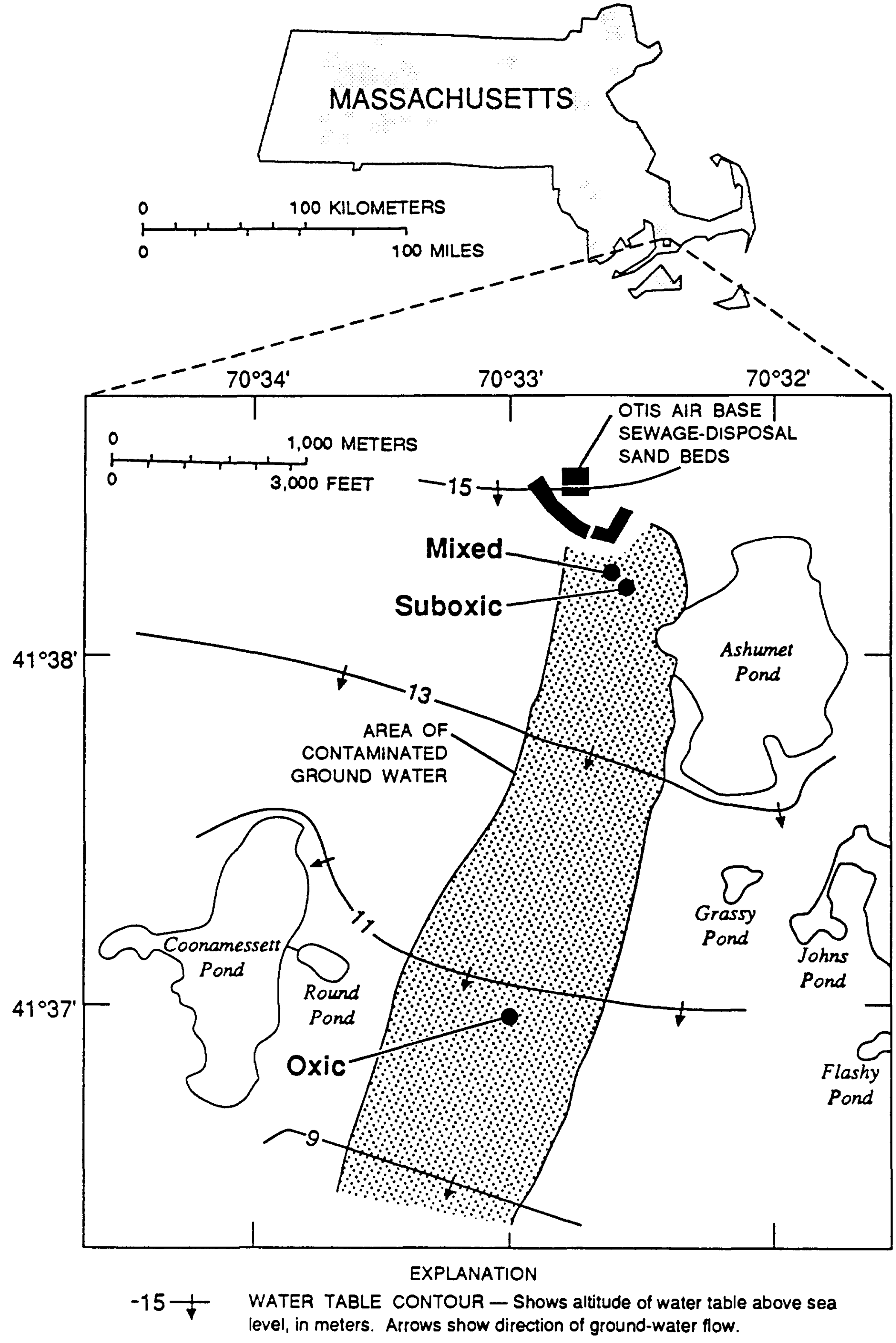
MASSACHUSETTS
0 100 KILOMETERS
0 100 MILES
70°34'
70°33'
70°32'
OTIS AIR BASE SEWAGE-DISPOSAL SAND BEDS
0 1,000 METERS
0 3,000 FEET
15
Mixed
Suboxic
41°38'
13
Ashumet Pond
AREA OF CONTAMINATED GROUND WATER
Grassy Pond
Johns Pond
11
Coonamessett Pond
Round Pond
41°37'
Oxic
Flashy Pond
9
EXPLANATION
-15
WATER TABLE CONTOUR — Shows altitude of water table above sea level, in meters. Arrows show direction of ground-water flow.

Figure 1. Location of the Mixed (site M), Suboxic (site S), and Oxic (site O) sites, sewage-disposal beds, water table, and sewage plume (stippled area).

Table 1. *Chemical characteristics of recharge zone at oxic site and sewage-contaminated zone at mixed and suboxic sites*

[Concentrations in micromolar except pH, which is on National Bureau of Standards pH scale]

Solute	Concentration	
	Recharge zone	Sewage-contaminated zone
Na	405	1,350
Ca	27	274
Mg	57	180
K	10	130
Cl	360	1,380
Sulfate	102	305
Nitrate	0	[1]650
Dissolved oxygen	250	[1].2
pH	5.0	6.0

[1] Nitrate and dissolved oxygen concentrations decrease with depth and reach zero deep in the plume (Smith and Duff, 1988).

Details of the procedures involved in performing and sampling the tracer tests are given in Davis and others (1991) and are summarized below. Ground water was pumped into acid-washed polyethylene bags. Tracers were added as preweighed powders. Target concentrations for the tracers in the 1988 tests were as follows: 1.9 millimolar Br^-, 100 µM (micromolar) Zn^{2+} (as Zn-EDTA complexes), 500 µM EDTA (as Zn-EDTA, calcium-(Ca)-EDTA, Mg-EDTA, complexes and H_2EDTA^{2-}), 100 µM CrO_4^{2-}, and 60 µM SeO_4^{2-}. NaOH was added to adjust the pH to 4.0. The volumes of the injectates were 400 L (liters). Tracer tests performed in 1989 involved slight modifications. Nickel (Ni), as Ni-EDTA complexes, was injected in addition to Zn-EDTA. Volumes of injectates ranged from 400 to 600 L. The pH values were adjusted to the ambient values--namely, 5.0 at site O and 6.0 at sites M and S. In all tracer tests, thermodynamic computations showed that all tracers were undersaturated with respect to hydroxides and salts formed with anions and cations listed in table 1.

Tracer tests at sites M and S were performed using parts of the large-scale array of multilevel samplers (MLS) described by LeBlanc and others (1991). At site M, the tracer cloud was injected into three tubes of an MLS with depths separated by 0.25 m (meters). Breakthrough curves were collected at various depths of MLS located 4 and 22 m downgradient from the injection well. At site S, the tracer cloud was injected into two tubes of an MLS that had a vertical separation of 0.51 m. Samples for constructing breakthrough curves were collected at an MLS located 10 m downgradient from the injection well.

Site O is located 2.3 kilometers downgradient from sites M and S, where a small cluster of MLS is located. The tracer cloud was injected into three tubes of an MLS; the tubes were 0.38 m apart. Samples for constructing breakthrough curves were collected at various depths of MLS located 2, 7, and 17 m downgradient from the injection well.

RESULTS

Breakthrough curves for Br and Zn at site M at an MLS 4 m downgradient from the injection well are shown in figure 3. These breakthrough curves are from the lower part of the tracer cloud; breakthrough curves from the upper part of the tracer cloud show elevated concentrations of Zn as a result of leaching of adsorbed Zn from the aquifer material by EDTA (Rea and others, 1991, this Proceedings). Breakthrough curves for the lower part of the tracer cloud at an MLS 22 m downgradient also show that the Zn and Br peaks coincide. Breakthrough curves from an MLS 10 m downgradient from the injection MLS at site S were similar to those shown for site M.

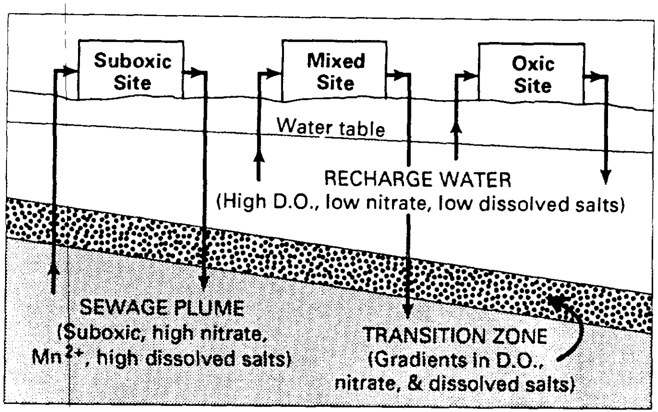
Suboxic Site
Mixed Site
Oxic Site
Water table
RECHARGE WATER
(High D.O., low nitrate, low dissolved salts)
SEWAGE PLUME
(Suboxic, high nitrate, Mn2+, high dissolved salts)
TRANSITION ZONE
(Gradients in D.O., nitrate, & dissolved salts)

Figure 2. Diagram illustrating how small-scale tracer tests at the Oxic, Mixed, and Suboxic sites exploited the vertical gradient in ground-water chemistry. D.O. stands for dissolved oxygen. Note that the diagram is not to scale.

Breakthrough curves for Br and Zn at site O, from an MLS 2 m downgradient from the injection well, are shown in figure 4. The data in figure 4 are for a single depth near the center of the tracer cloud. Breakthrough curves for other depths show the same trends.

Deviations from ambient pH values were observed during breakthrough of tracers at site O. The pH values during breakthrough corresponding to the curves shown in figure 4 are presented in table 2. The pH decreased from the ambient value of 4.9 to 4.3. No such deviation from ambient pH occurred at sites M or S. This decrease in pH during breakthrough was probably caused by incomplete neutralization of the excess acid from the injectate in the poorly buffered aquifer, although chemical interactions between the constituents of the tracer cloud and aquifer material also could have affected the pH.

In addition to breakthrough curves for Br and Zn, a breakthrough curve for "excess-metals" is shown in figure 4. This is shown to depict qualitatively the breakthrough of EDTA. EDTA was not determined until several months after the tracer test had been completed. The results of the EDTA determinations suggested that some degradation of EDTA may have occurred, although other analytical problems may have caused the discrepancies that were observed. In order to determine qualitatively when EDTA had broken through, the concentrations of dissolved iron (Fe), aluminum (Al), Zn, Mn, Ca, in excess of their background concentrations were summed. The sum of the excess concentrations of these metals was divided by the EDTA concentration in the injectate to obtain the excess-metals breakthrough curve shown in figure 4. During breakthrough of the low-pH part of the tracer cloud, some of the dissolved Al may have been present as Al^{3+}, $Al(OH)^{2+}$, and $Al(OH)_2^+$ rather than EDTA complexes. This is discussed further below. Ultraviolet (UV)

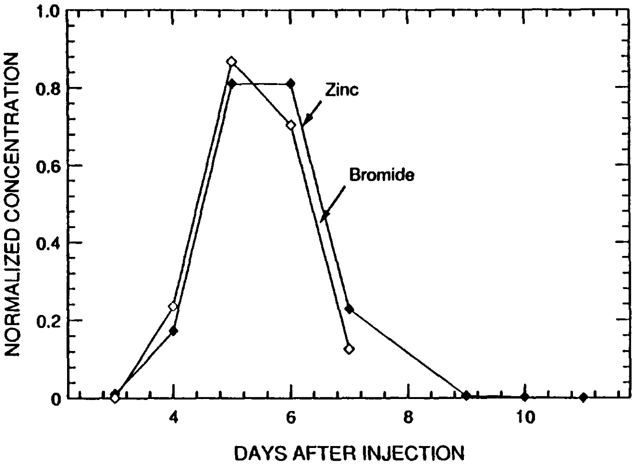

Figure 3. Breakthrough curves 4 meters downgradient from injection multilevel sampler at the Mixed site. The sampling port was at an altitude of 10.6 meters above sea level, which was in the lower part of the injected tracer cloud.

absorbances determined in the course of attempting to quantify the EDTA concentration showed that breakthrough of EDTA probably began 1 day later than indicated by the excess-metals curve; the peak and tail of the excess-metals curve, however, are in good agreement with the UV absorbance determinations.

In subsequent tracer tests, EDTA was determined within a few weeks of collecting the ground-water samples. The analytical results showed that breakdown of EDTA in the aquifer did not occur. Previous investigations have shown that EDTA is resistant to breakdown in ground water (Means and others, 1980).

The results of the tracer tests at site O show that both Zn and EDTA were retarded. The peak for EDTA occurs 1 to 2 days after that for Br. Breakthrough of Zn peaked 4 to 5 days after Br and 2 to 3 days after EDTA.

DISCUSSION

Tracer test results showed that Zn transport was markedly different in the recharge and sewage-contaminated zones (see figs. 3 and 4). Zn was conservative in the sewage-contaminated zone. In the recharge zone, Zn was greatly retarded.

Conservative transport of Zn in the sewage-contaminated zone is consistent with transport of Zn as Zn-EDTA complexes. Breakthrough of EDTA, as estimated from excess-metals breakthrough curves, coincides with that of Br and Zn at site M (data not shown). Speciation computations using measured concentrations of Fe, Al, Ca, and Zn and EDTA concentrations calculated by assuming conservative transport of EDTA-containing species showed that 100 percent of dissolved Zn was present as Zn-EDTA complexes. Laboratory determinations of the extent of adsorption of Zn onto Cape Cod aquifer material (CCAM) collected from site M in the presence of EDTA showed that Zn was not adsorbed near pH 6 in the presence of excess EDTA (Davis and others, 1991). Thus, at pH 6, Zn remains completely tied up as Zn-EDTA complexes, which do not adsorb onto the aquifer material (Davis and others, 1991).

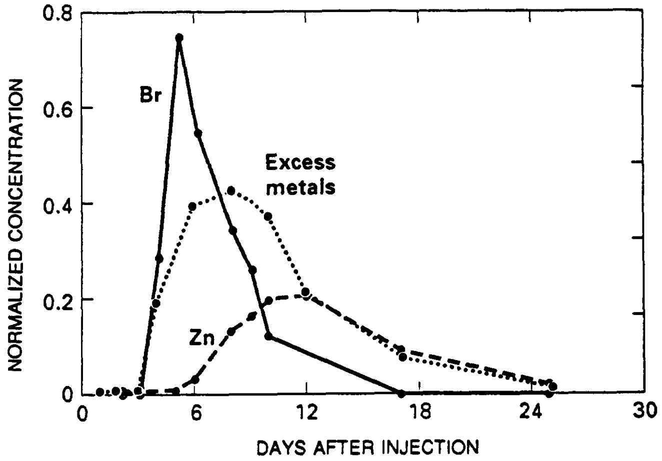

Figure 4. Breakthrough curves for bromide, zinc, and excess metals 2 meters downgradient from injection multilevel sampler at Oxic site (recharge zone). Breakthrough curves shown came from near the vertical center of injected tracer cloud, which was at an altitude of 6.1 meters above sea level.

Table 2. *pH values during breakthrough of tracers at oxic site, 2 meters downgradient at an altitude of 6.1 meters above sea level*

[pH values on National Bureau of Standards pH scale; --, denotes no data]

Days after injection	pH	Bromide, normalized concentration
1	4.9	0
2	4.9	0
3	4.9	.01
4	4.8	.29
5	4.6	.75
6	4.4	.55
9	4.3	.26
10	4.6	.12
12	5.0	--

Considerable retardation of Zn was observed in the recharge zone (fig. 4), probably because some or all of the Zn was displaced from EDTA complexes to form the Zn^{2+} species, which is strongly adsorbed onto CCAM (Rea and others, 1991, this Proceedings). Batch experiments of Zn adsorption on CCAM showed that, at pH values below 5.5, the extent of Zn adsorption was identical in the presence and absence of EDTA (Davis and others, 1991). The concentration of dissolved Fe exceeded that of EDTA below pH 5.5 but was much less than that of EDTA above pH 5.5. Equilibrium speciation computations predict that, in solutions with equimolar concentrations of Fe(III), EDTA, and Zn, all of the EDTA would be tied up as Fe-EDTA complexes and Zn would be present as the Zn^{2+} species. According to this proposed mechanism, retardation of Zn at site O resulted from displacement of Zn from EDTA complexes by Fe(III) leached from the aquifer material and adsorption of free Zn^{2+}.

Without independent determinations of the concentration of EDTA it is not possible to compute the speciation of Zn during breakthrough at site O. The excess-metals summation is only an approximate measure of the EDTA concentration. The pH values of the tracer cloud initially decreased during breakthrough and appeared to have reached maximum deviation from ambient pH at the same time as the peak in the excess-metals breakthrough curve. The solubilities of hydrous Al and Fe oxides increase with decreasing pH (Baes and Mesmer, 1976). Thus, during breakthrough of the low-pH part of the tracer cloud, some of the dissolved Al and Fe may have been present as uncomplexed cations. However, during the tail of the excess-metals breakthrough curve, where the pH had returned to 5.0, the concentrations of dissolved Fe exceeded those predicted by the solubility of ferrihydrite, which is the most soluble hydrous ferric oxide, in the absence of EDTA. This supports the assumption that Fe and other excess-metals were transported as EDTA complexes rather than as free metal ions after the pH had returned to the ambient value. Comparison of the excess-metals concentrations with estimates of EDTA concentrations from UV-absorbance measurements suggests that breakthrough of EDTA occurred 1 day later than that indicated by the excess-metals breakthrough curve but that the peak and tail appeared to be in good agreement. The excess-metals breakthrough curve was therefore assumed to represent breakthrough of EDTA qualitatively but could not be used for quantitative purposes.

Some caveats to the interpretation presented above should be mentioned. First, the batch experiments of Davis and others (1991) were performed at an ionic strength of 0.1 molar, which greatly exceeds the ionic strengths of both the recharge and sewage-contaminated zones. Higher values of ionic strength inhibit adsorption of weakly adsorbing species but have little effect on the adsorption of strongly adsorbing species (Davis and Kent, 1990). Zn-EDTA species are weakly adsorbing anions, whereas the Zn^{2+} species is a strongly adsorbing cation. Second, metal-EDTA complexes do not necessarily dissociate rapidly (Hering and Morel, 1988; 1989). Thus, even if thermodynamic calculations indicated that the concentration of Fe(III) was high enough to displace Zn from EDTA complexes, sluggish dissociation kinetics could have caused Zn to remain tied up as EDTA complexes. Furthermore, there was an excess of Zn over EDTA in the batch experiments, but there was a large excess of EDTA over Zn in the tracer tests. The low EDTA:Zn ratio in the batch adsorption experiments could have led to more favorable dissociation kinetics in the batch experiments than in the tracer tests. Conversely, the greater duration of the tracer test should favor achievement of equilibrium between solution species.

Another possible cause of the observed retardation of Zn is the adsorption $ZnEDTA^{2-}$, which is the dominant Zn-EDTA complex under the conditions of the tracer test. Breakthrough curves for chromate (Anderson and others, 1991, this Proceedings), and selenate (Davis and others, 1991) bear striking similarities to that for Zn. Selenate is a weakly adsorbing divalent anion in the pH range 4.3 to 5.0 (namely SeO_4^{2-}); chromate is a weakly adsorbing monovalent anion (namely, $HCrO_4^-$). The lower concentrations of anions in the recharge zone at site O as compared to the sewage-contaminated zone at site M (table 1) should enhance the adsorption of weakly adsorbing anions such as $ZnEDTA^{2-}$ in the recharge zone (Anderson and others, 1991, this Proceedings). Laboratory adsorption experiments performed in systems with synthetic oxides have shown that $ZnEDTA^{2-}$ adsorbs weakly on Fe and Al oxides at pH values near 5.0 (Bowers and Huang, 1986; 1987; Huang and others, 1988). Thus, it is possible that the retardation observed could have been caused by adsorption of Zn-EDTA complexes.

A third hypothesis for differences in transport of Zn in the recharge and sewage-contaminated zone should be considered. It is possible that the adsorptive capacity for aquifer material from the oxic, recharge zone is much greater than that from the suboxic, sewage-contaminated zone. The mildly reducing conditions in the sewage-contaminated zone could cause slower rates of formation, or even dissolution, of hydrous Fe and Mn coatings, which have large adsorptive capacities. This topic is currently being addressed in a separate research project (Fuller and others, 1991, this Proceedings). However, two arguments can be made against this hypothesis. First, chemical extractions designed to quantify Fe and Mn oxide coatings failed to show major differences between aquifer material from the oxic and suboxic zones. Second, the redox conditions in the suboxic zone do not appear to be sufficiently reducing to allow for large-scale reduction of Fe(III) oxides (Davis and others, 1991).

The importance of understanding the speciation of Zn during breakthrough prompted an additional set of tracer tests in 1989. Two modifications in procedure were adopted in order to determine speciation. First, ground-water samples were analyzed for EDTA within a few weeks of collection to reduce the degradation observed in the 1988 samples. Knowing the concentration of EDTA as well as those of the metals with which it forms complexes will allow us to compute the equilibrium speciation in the system. Second, ground-water samples were subjected in the field to a protocol designed to separate cationic species of metal ions from EDTA complexes. The procedure involved passing a ground-water sample through a Chelex[2] membrane. Chelex is a cation exchanger that has a high affinity for multivalent cations while having no affinity for anions. Therefore, cations such as Zn^{2+} and $Fe(OH)_2^+$ should be retained by the Chelex while anionic complexes such as $ZnEDTA^{2-}$ and $FeEDTA^-$ should pass through the membrane. This was verified for Zn and Fe(III) in laboratory experiments performed with artificial ground water. Comparison of the concentrations of metals in ground-water samples passed through Chelex membranes with the total concentrations in the ground water will allow us to determine if metals were present as cations or anionic EDTA complexes.

CONCLUSIONS

It is clear from these results that understanding metal ion speciation is central to understanding adsorption and transport in situations where a complexing ligand is present. In most systems, it will be necessary to determine the concentrations of all cations capable of competing with target metal ions for the ligands that are present. Changes in aquifer chemistry encountered along a ground-water-flow path can affect speciation and, therefore, transport. In many field situations involving transport of metal ions, it will be necessary to focus attention on determining metal ion speciation in addition to total concentrations, that is, the sum of concentrations of all dissolved species. Accurate modeling will require incorporation of speciation and adsorption.

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[2] The use of brand, firm, or trade names in this paper is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

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SPATIAL VARIABILITY OF GEOCHEMICAL AND HYDROLOGIC PROPERTIES OF SUBSURFACE MATERIALS IN A SAND AND GRAVEL AQUIFER, CAPE COD, MASSACHUSETTS

By Christopher C. Fuller[1], Jennifer A. Coston[1], Kathryn M. Hess[2], *and* James A. Davis[1]

ABSTRACT

The effect of spatial variability in geochemical and hydrologic parameters on the transport of surface-reactive solutes in ground-water systems is being investigated in a shallow, sand and gravel aquifer on Cape Cod, Massachusetts. The focus of this study is to identify the geochemical properties controlling metal-ion sorption and to describe their spatial variability. The spatial variability of hydraulic conductivity estimated from grain-size distribution measurements also is being studied. The results will be used in conjunction with tracer-test studies of metal transport conducted at this site to develop coupled solute transport and reaction models that incorporate the observed spatial variability in geochemical properties used to estimate sorbent abundance, metal sorption coefficients, and hydraulic conductivity. This paper outlines the objectives and approach of this research study. Sixty meters of core have been collected and the initial laboratory phase of this research has recently begun.

INTRODUCTION

The spatial variability of parameters used in models for solute transport in ground water are of significance in the simulations of solute movement. Variability of hydraulic conductivity has been shown to be a primary cause of macroscale dispersion (Garabedian and others, 1988). Variability in geochemical properties are thought to further increase dispersion of reactive solutes as they are transported through an aquifer. A study has been initiated to investigate the effects of spatial variability of geochemical and hydraulic properties at the site of a large-scale and several small-scale, natural gradient tracer tests (Davis, Kent, Rea, Garabedian, and Anderson, 1991; Davis, Kent, Rea, Maest, and Garabedian, 1991; Le Blanc and others, 1991) on Cape Cod, Mass. (fig. 1).

The concentrations of many minor elements in ground water such as heavy metals are often undersaturated with respect to pure solid phases of known structure and composition, and the aqueous concentrations of these elements are thought to be controlled by sorption reactions (Davis and Hayes, 1986). Adsorption-desorption reactions of metal ions with the porous medium need to be incorporated within models of metal transport. Typically, these reactions are represented by sorption coefficients that quantify the distribution of metal ions between water and mineral phases by either an empirical or pseudothermodynamic approach (Davis and Kent, 1990). As observed for hydraulic conductivity (Hess and others, 1989), the geochemical properties of the porous medium that control metal adsorption are believed to be spatially variable. The scope of this study is to characterize these geochemical heterogeneities and to investigate their effects on metal transport in aquifers. The hydrology and geochemistry of this shallow, unconfined aquifer, which consists of glacial outwash sands and gravels, are described elsewhere (LeBlanc, 1984; Garabedian and others, 1988; Davis, Kent, Rea, Garabedian, and Anderson, 1991; Davis, Kent, Rea, Maest, and Garabedian, 1991). This paper outlines the objectives and approaches to be used in this study.

STUDY OBJECTIVES

The objectives of this study are to:

(1) Understand the important chemical-physical properties of subsurface material, such as iron and manganese content and surface area, that control the adsorption of selected heavy metals at this site;

(2) Determine the spatial variability of physical and geochemical characteristics of subsurface material that affect adsorption-controlled metal-ion transport, including hydraulic conductivity determined from its correlation with grain-size distribution (Wolf and others, 1991), heavy metal adsorption coefficients, and a geochemical "indicator" of metal-absorbent abundance; and

(3) Understand the effect of spatial variability on transport-model parameters, such as hydraulic conductivity and metal adsorption coefficients, by employing statistical analyses of the variabilities observed in the investigated physical and geochemical properties.

APPROACH

Laboratory studies

Detailed batch adsorption experiments are being conducted on subsurface material collected from the tracer-test site to determine the principal minerals or phases in the aquifer sands that are responsible for the sorption of two metal ions, zinc and lead (Zn^{2+}, Pb^{2+}). These experiments are being conducted under similar chemical conditions to those found in the aquifer, by methods similar to those of Fuller and Davis (1987). The experiments are being conducted on aquifer materials composited from intervals of cores collected below a zone of zinc contamination (Rea and others, 1991, this Proceedings). These experiments include kinetic and quasi-equilibrium aspects of sorption, such as time dependence of adsorption, reversibility of adsorption, pH dependency, and sorption capacity. The sand fractions investigated include grain-size fractions; magnetic, paramagnetic, and diamagnetic fractions; sand leached with hydroxylamine hydrochloride to remove poorly crystalline coatings; and mineral fractions manually separated by optical

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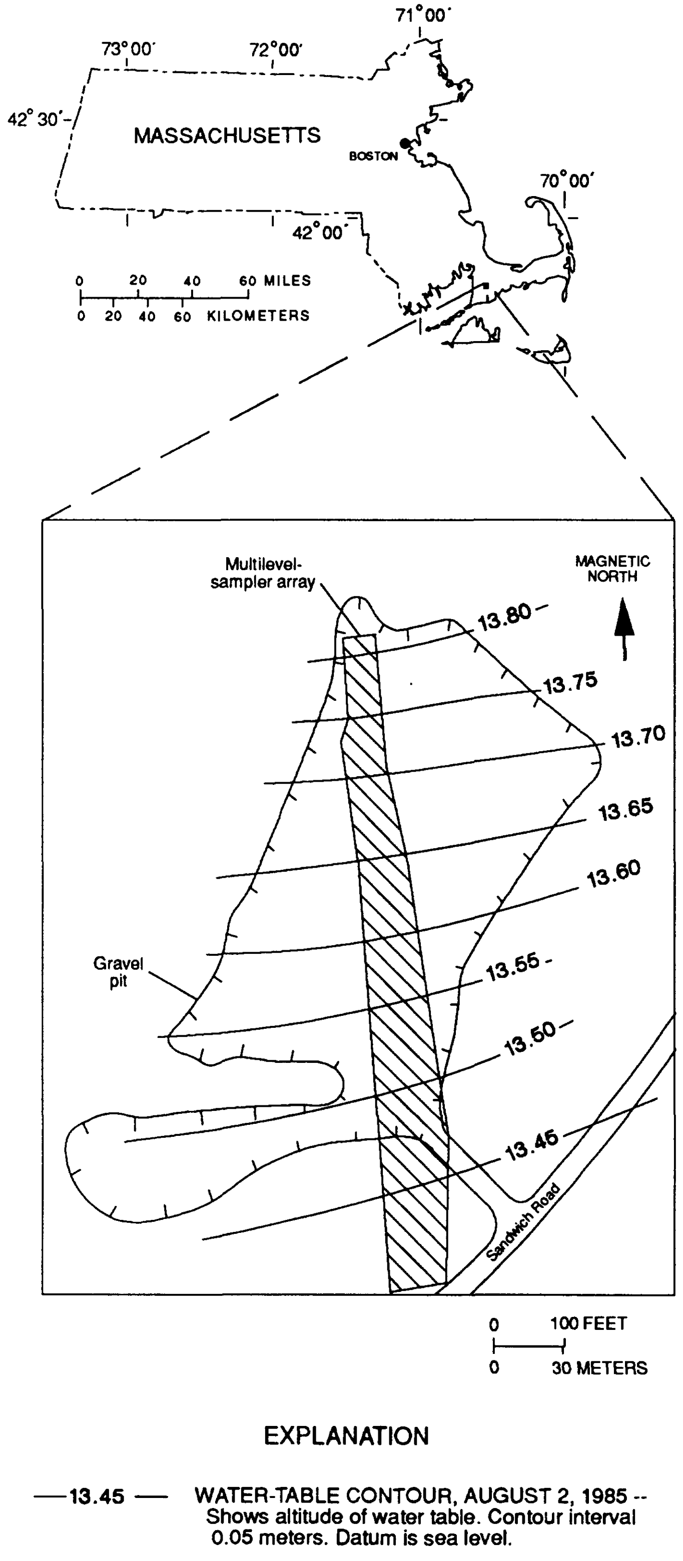
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MASSACHUSETTS
BOSTON
70°00'
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0 20 40 60 MILES
0 20 40 60 KILOMETERS
Multilevel-sampler array
MAGNETIC NORTH
13.80
13.75
13.70
13.65
13.60
13.55
13.50
13.45
Gravel pit
Sandwich Road
0 100 FEET
0 30 METERS
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.)

microscopy (Fuller and Davis, 1987). Physical and chemical properties relevant to metal sorption are being determined, including surface area and microporosity; bulk mineralogy by X-ray diffraction; and surface analysis by scanning electron microscopy with elemental surface analysis (SEM-EDAX) of individual treated and untreated sand grains. Correlations between metal sorption variability and geochemical properties of bulk sand and various fractions will then be examined. It is expected that a single mineral or suite of minerals that dominates the sorption reactions can be identified. The spatial variability of this geochemical "indicator" will then be determined in the aquifer along with the variability of metal sorption and hydraulic conductivity.

Field Sampling

Six 4.5-m (meter)-long cores were collected along a 16-m-long transect parallel to ground-water flow in August 1990 to determine correlation scales of metal sorption and the geochemical "indicator." The correlation scales for metal sorption and the geochemical "indicator" are unknown; therefore, the horizontal spacing of the transect cores and the vertical subsections were based on the correlation scales of the hydraulic-conductivity distribution from an adjacent transect (Hess and others, 1989). Variability in hydraulic conductivity, determined from grain-size-distribution measurements, will be used to compare the results of this study to those observed by Hess and others (1989). Six additional cores were collected at random locations around the downgradient two-thirds of the tracer-test array. The separation of these cores ranged from 14 to 135 m, and were located 16 to 100 m from the transect cores. The top of all cores was 12.8 m above sea level, or about 0.5 to 1.5 m below the water table. The depth range of the cores was chosen to bracket the transition from oxygenated recharge water to the suboxic, high specific conductance water of the underlying contaminated ground water (Smith and others, 1991), and to be within the depth range of nearby multilevel samplers (MLS). Water samples collected in August 1990 at MLSs adjacent to coring sites indicated that the dissolved oxygen gradient, or "redox boundary," deepened to the south (downgradient) and to the east. As a result, the cores collected bracketed the redox boundary, possibly providing additional variability in the metal sorption properties of the aquifer material, such as iron and manganese oxide coatings. All cores were collected using a modified wire-line piston corer in 1.5-m-long sections (Zapico and others, 1987).

Vertical subsamples from both the transect and randomly located cores will be used for variogram analysis of hydraulic conductivity, as determined by grain-size distribution (Wolf, 1988; Wolf and others, 1991), and of the geochemical "indicator" of metal-sorbent abundance based on the results of the laboratory study. In addition, laboratory batch sorption experiments will be conducted on these same subsamples. The spatial variability of empirical sorption coefficients will be determined from these data with subsequent variogram analysis.

Statistical Analysis of Hydrologic and Geochemical Parameters

The data collected will allow a detailed statistical analysis of correlations between hydraulic conductivity and geochemical properties that affect metal sorption. Correlations among grain size, sorption coefficients, and the geochemical "indicator" will be examined. The distribution of the measured geochemical variables within the tracer-test area will be described by the data set collected from the widely separated core locations. Directional variogram analyses of grain size, adsorption, and adsorbent abundance will allow comparisons to be made of correlation scales of the hydrologic and geochemical properties of the aquifer. The results may lead to an application of stochastic theory to describe sorption-controlled metal transport (Garabedian and others, 1988).

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MOBILITY OF ZINC IN A SEWAGE-CONTAMINATED AQUIFER, CAPE COD, MASSACHUSETTS

By B.A. Rea[1], D.B. Kent[1], Denis R. LeBlanc[2], and J.A. Davis[1]

ABSTRACT

Disposal of treated sewage effluent into the sand and gravel aquifer on Cape Cod, Massachusetts, has resulted in contamination of the aquifer with zinc (Zn). At sites up to 350 meters downgradient from the disposal site, a zone of elevated concentrations of dissolved Zn is supported by a reservoir of adsorbed Zn. The contamination is limited to a 1- to 2-meter-thick zone at the upper margin of the sewage plume. At greater depths, the sewage plume is devoid of Zn, indicating that processes upgradient have lead to immobilizaton of Zn. Preliminary evidence supports the hypothesis that adsorption onto the aquifer material, which is complete at pH values characteristic of the sewage-contaminated zone, is the process responsible for immobilization. If true, there is a large reservoir of immobilized Zn in the vicinity of the disposal bed that could be mobilized by future changes in the aquifer chemistry.

INTRODUCTION

Fifty years of land application of effluent from the Otis Air Base sewage-treatment facility on Cape Cod, Mass., has created a plume of sewage-contaminated ground water that is more than 4 km (kilometers) long and 26 m (meters) thick (fig. 1) (LeBlanc, 1984). The presence of the sewage plume gives rise to a vertical gradient in ground-water chemistry (fig. 2). A recharge zone derived from precipitation overlies the sewage plume. The recharge zone is characterized by high concentrations of dissolved oxygen, low pH values, and low concentrations of dissolved salts (Kent and others, 1991, this Proceedings). The sewage-contaminated zone has low concentrations of dissolved oxygen (suboxic), elevated concentrations of dissolved salts, and higher pH values than the overlying recharge zone (for detailed list of chemical characteristics, see Kent and others, 1991, this Proceedings). Between the recharge and sewage-contaminated zones is a transition zone characterized by steep gradients in concentrations of dissolved salts and oxygen. Recently, we discovered zinc (Zn) contamination within the transition zone. This paper is a preliminary report of the results of our investigations into the distribution of Zn contamination and mobility of Zn at the site.

The location of the study area is shown in figure 1. The area of most intensive study is between the disposal beds and Ashumet Pond. This area is densely instrumented with multilevel sampling devices (MLS) (LeBlanc and others, 1991). The detailed vertical resolution provided by these MLS has facilitated the characterization of Zn contamination. The aquifer in this region is highly permeable sand and gravel with ground-water velocities in the range 0.2 to 0.5 m per day.

METHODS

Zn transport was investigated using both laboratory and field experiments. Laboratory experiments were designed to evaluate Zn adsorption onto the aquifer material. Field work included characterization of aquifer chemistry and performing small-scale tracer tests.

Zn adsorption was investigated in batch experiments on aquifer material collected from the field site. A detailed description of methods is given in Davis, Kent, Rea, Maest, and Garabedian, (1991). Cape Cod aquifer material (CCAM) from the recharge zone was collected using the method of Zapico and others (1987). Core 18 came from the Mixed site and core 20 from the Suboxic site (fig. 1). The cores were frozen for overnight transport to Menlo Park, Calif., air-dried, and seived to remove material greater than 2 millimeters. The dried material was stored under ambient conditions. Description of the mineralogy and chemistry of the material is given in Barber (1987; 1990). Adsorption experiments were performed in centrifuge tubes containing 0.1 molar $NaNO_3$ at 22 °C (degrees Celsius), with about 10 grams of sand suspended in 22.5 cubic centimeters of electrolyte. The suspensions were mixed by rotating end-over-end. An aliquot of Zn stock solution was added to each suspension to achieve a total concentration of 5 μM (micromolar); some of the tubes contained radiolabled ^{65}Zn. The pH value of each suspension was adjusted by adding HNO_3. The suspensions were allowed to equilibrate for 18 hours, after which they were centrifuged and the supernatant solution sampled. Zn adsorption was determined by measuring the removal of Zn from the suspension using gamma spectrometry for suspensions with ^{65}Zn or flame atomic absorption spectrometry for those without the radioactive Zn.

Chemical extractions were done on CCAM from the Mixed (core 18) and Suboxic (core 20) sites (Davis, Kent, Rea, Maest, and Garabedian, 1991). Extractions were done using the hydroxylamine hydrochloride method of Chao and Zhou (1983). The method is designed to dissolve manganese (Mn) oxides and poorly crystalline hydrous ferric oxides but also leaches all Zn that is adsorbed to constituents of the CCAM.

Detailed procedures for collecting and analyzing ground-water samples are given in Davis, Kent, Rea, Maest, and Garabedian, (1991). Water samples were collected from MLS with peristaltic pumps. Concentrations of most metal ions were determined by inductively coupled plasma (ICP) spectrometry on acidified samples. Specific conductance (κ), dissolved oxygen (DO) concentrations, and pH values were measured in the field as described in Davis, Kent, Rea, Maest, and Garabedian (1991).

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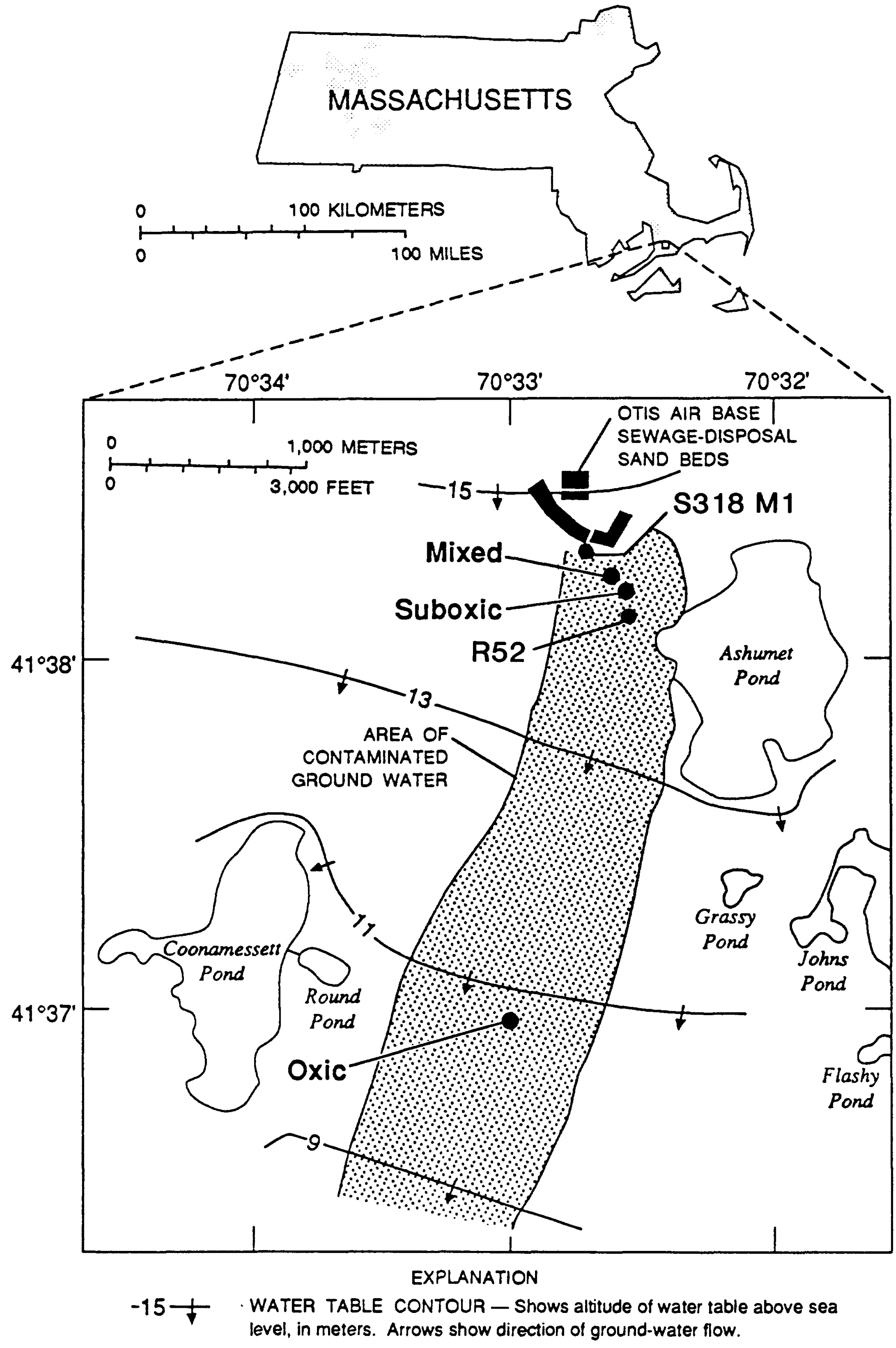
MASSACHUSETTS
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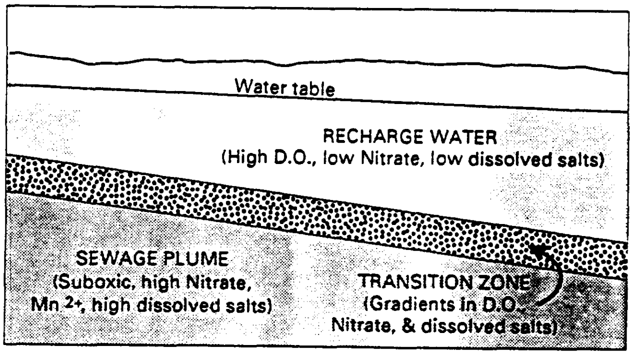
3,000 FEET
OTIS AIR BASE
SEWAGE-DISPOSAL
SAND BEDS
15
S318 M1
Mixed
Suboxic
R52
13
AREA OF
CONTAMINATED
GROUND WATER
11
9
Oxic
Ashumet Pond
Grassy Pond
Johns Pond
Flashy Pond
Coonamessett Pond
Round Pond
EXPLANATION
-15
WATER TABLE CONTOUR — Shows altitude of water table above sea level, in meters. Arrows show direction of ground-water flow.

Figure 1. Location map showing the sewage disposal beds, sewage plume, water-table contours, and sites referred to herein, including the Mixed, Suboxic, and Oxic sites, and multilevel samplers at S318 M1 and row 52 (R52) of the large scale array.


Water table
RECHARGE WATER
(High D.O., low Nitrate, low dissolved salts)
SEWAGE PLUME
(Suboxic, high Nitrate, Mn 2+, high dissolved salts)
TRANSITION ZONE
(Gradients in D.O., Nitrate, & dissolved salts)

NOT TO SCALE

Figure 2. Schematic diagram illustrating the vertical zonation in ground-water chemistry caused by the presence of the sewage plume. Recharge water has high concentrations of dissolved oxygen (DO), and low concentrations of nitrate and dissolved salts. The sewage plume is suboxic, with dissolved manganese (Mn^{2+}), nitrate, and high concentrations of dissolved salts.

A small-scale natural-gradient tracer test was performed at the Mixed site (Davis, Kent, Rea, Maest, and Garabedian, 1991; Kent and others, 1991, this Proceedings). Approximately 400 liters of ground water were withdrawn from the Oxic site (fig. 1) into a polyethylene bag. Tracers were dissolved in the ground water and the mixture was injected into the sewage-contaminated zone at the Mixed site. Tracers included 1.9 millimolar bromide (Br), which is transported conservatively in the aquifer (Garabedian and others, 1991), 500 µM ethylenediaminetetracetic acid (EDTA as H_2EDTA^{2-}, $ZnEDTA^{2-}$, and $CaEDTA^{2-}$), and 100 µM Zn (as $ZnEDTA^{2-}$). Data for constructing breakthrough curves were obtained at MLS, 4 m and 22 m downgradient from the injection MLS.

RESULTS

Zinc Adsorption onto Cape Cod Aquifer Material

Zn adsorption onto CCAM is shown in figure 3. The extent of Zn adsorption increases with increasing pH until all added Zn is adsorbed at pH 7.0. This pH dependency is typical for cation adsorption onto minerals and results from the release of protons that accompanies the chemical reaction between cations and surface sites (Davis and Kent, 1990). The results shown in figure 3 were obtained at a solid:liquid (S:L) ratio of 445 g/L (grams per liter). The solid:liquid ratio in the aquifer is 4,000 g/L, which was calculated from a porosity of 0.4 (LeBlanc, 1984) and a solid-phase density of 2.65 g/cm^3 (grams per cubic centimeter) (density of quartz, taken as the average density of unconsolidated aquifer material from Freeze and Cherry, 1979).

Adsorption at a S:L ratio of 4,000 g/L was estimated using a surface complexation model (SCM). A variety of SCMs are available and could be applied (Davis and Kent, 1990). We used a simple, nonelectrostatic SCM, whereby the adsorption of Zn on CCAM was described by a single chemical reaction between Zn and adsorption sites (SOH):

$$SOH + Zn^{2+} = SOZn^{+} + H^{+}. \qquad (1)$$

Adsorption was described mathematically using the mass action expression for equation 1:

$$\frac{[\,SOZn^{+}\,][\,H^{+}\,]}{[\,SOH\,][\,Zn^{2+}\,]} = K_{ap}\ , \qquad (2)$$

where the square brackets denote concentration, in moles per liter, and K_{ap} is the apparent equilibrium constant, which is a measure of the affinity of Zn for surface sites. The electrostatic term resulting from bringing Zn^{2+} through the electrical double layer was ignored; hence, fitting the data with this SCM involves evaluating two interdependent parameters--that is, the total concentration of adsorption sites (SOH_{tot}) and K_{ap}. The SOH_{tot}, which is the sum of [SOH] and [$SOZn^{+}$], was calculated from 445 g/L (the S:L ratio) and an assumed adsorption site density of 3.84 micromoles per square meter (Davis and Kent, 1990) and a specific surface area of 1 square meter per gram. A value of $K_{ap} = 10^{-2.6}$ gives an excellent fit to the data, which is shown in figure 3 as the solid curve. The adsorption in the aquifer at a S:L ratio of 4,000 g/L was computed using the same adsorption-site density and K_{ap}. The results of the SCM calculation for the higher S:L ratio are shown in figure 3 as the dashed curve. Several factors cast uncertainties on such linear extrapolations to higher S:L ratio (Davis and Kent, 1990), so the dashed curve represents only a rough estimate of adsorption at the S:L ratio found in the aquifer.

Most of the minerals present in CCAM possess proton-donor sites capable of adsorbing Zn. The most abundant minerals such as quartz and feldspars, the accessory minerals such as hornblende, and trace minerals present as coatings such as ferrihydrite and hydrous Mn oxides all possess proton-donor

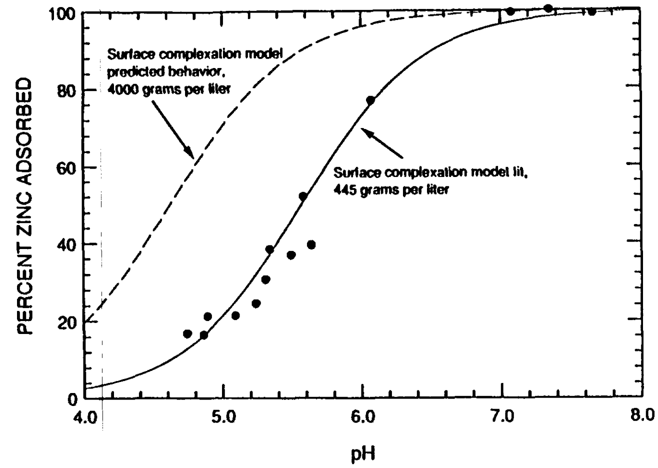


Figure 3. Zinc adsorption on Cape Cod aquifer material. Solid circles: results of batch experiments performed in 0.1 molar background electrolyte at 22 degrees Celsius in the presence of 445 grams of aquifer material per liter of solution and total concentration of zinc of 5 × 10^{-6} molar. Solid curve: fit of nonelectrostatic surface complexation model to data at 445 grams per liter (see text). Dashed curve: predicted adsorption at 4,000 grams per liter, solid: liquid ratio in aquifer.

sites. The relative importance of a specific mineral's contribution to Zn adsorption depends on the abundance of its surface sites compared to other solids and the affinity of its surface sites for Zn--that is, the K_{ap}. Fractional adsorption edges on single minerals are typically much steeper than those for CCAM (fig. 3). Therefore, it appears that the adsorption edge is a composite of two or more types of surface sites with different affinities for Zn. It is likely that weathering products, such as ferrihydrite and Mn-oxide minerals, dominate adsorption properties because (1) they form coatings on primary quartz and feldspar grains, thus blocking adsorption sites on these minerals, (2) have much larger reactive surface areas than do the primary grains, and (3) possess surface sites with higher affinities for adsorption of Zn and other metal ions than do the types of surface sites found on quartz (Davis and Kent, 1990). Differences in adsorption properties may exist between CCAM from the oxic recharge zone and suboxic sewage-contaminated zones. Weathering products are expected to be less abundant in CCAM from the suboxic zone than from the oxic zone because of slower rates of formation and possibly even reductive dissolution in response to the mildly reducing conditions (Davis, Kent, Rea, Maest, and Garabedian, 1991). These issues are being addressed by ongoing research projects (Fuller and others, 1991, this Proceedings).

Zinc contamination in the aquifer

Vertical profiles of several water-quality characteristics at the Mixed site are shown in figure 4. The pH values increase from about 5.4 in the recharge zone to nearly 6.5 in the upper part of the sewage plume. The concentrations of dissolved salts, as illustrated by specific conductance and Ca concentration, increase from the recharge zone to the sewage plume. Dissolved oxygen concentrations decrease from the recharge zone to the plume. The upper part of the sewage plume is suboxic, with dissolved oxygen concentrations of about 0.2 µM. Dissolved Mn, indicating the presence of Mn(II), was observed in the suboxic zone, but neither Fe(II) nor dissolved sulfide was detected at any of the depths shown in figure 4. These observations corroborate that the conditions are suboxic rather than anoxic (Davis, Kent, Rea, Garabedian, and Anderson, 1991, this Proceedings). The data presented in figure 4 indicate that the transition zone constitutes the upper margin of the zone of sewage plume, which is characterized by gradients in dissolved salts (K, Ca, and so forth) and DO (fig. 2).

A peak in the concentration of dissolved Zn is observed in a plot of Zn concentration with depth (fig. 4C). This peak is associated with the upper margin of the sewage plume. The low Zn concentrations at shallow depths below the water table in figure 4C are insignificant and probably represent contamination during sampling. A similar peak in dissolved Zn was seen at the Suboxic site (fig. 1), where it was also associated with the upper margin of the plume.

Consideration of the adsorption of Zn onto CCAM (fig. 3) shows that the small concentrations of dissolved Zn in the transition zone are supported by a resevoir of adsorbed Zn. The pH range across the region containing the peak in dissolved Zn is 5.5 to 6.0 (fig. 4A). Throughout this pH

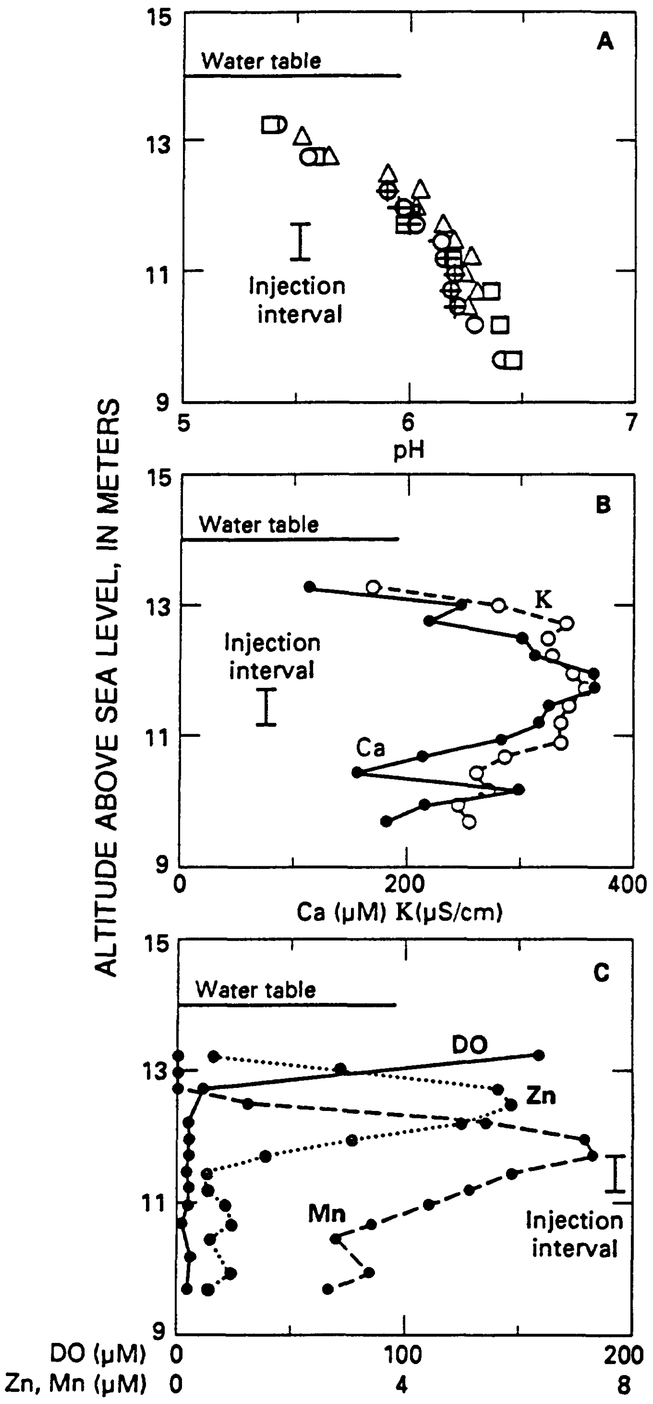


Figure 4. Vertical profiles of ground-water chemistry at the Mixed site. Injection interval shows the depths at which ground water with tracers was injected at this site. (A) pH as a function of depth. Different symbols denote different multilevel sampling devices illustrating constancy of conditions. (B) Calcium (Ca) and specific conductance (K). (C) Dissolved oxygen (DO), manganese (Mn), and zinc (Zn).

range, Zn was predicted to adsorb extensively on CCAM (dashed curve in fig. 3). Extractions of core material collected from the Mixed (core 18) and Suboxic (core 20) sites corroborate this conclusion (fig. 5); the peak in extractable Zn is present across the same depth range as the peak in dissolved Zn. Comparison of the highest dissolved Zn concentration of 5 μM ([Zn_{max}]) with the highest extractable Zn concentration of 0.6 micromole per gram (Zn_{ex}) indicates that 98 percent of the Zn is adsorbed.

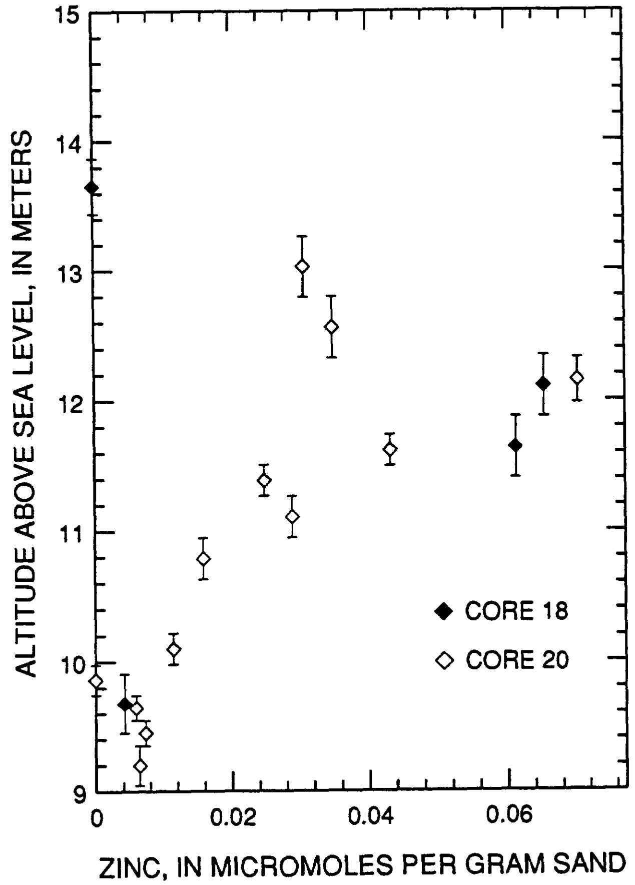


Figure 5. Results of hydroxylamine HCl extractions of Cape Cod aquifer material collected from Mixed site (core 18) and Suboxic site (core 19).

This value was computed using the equation:

Percent Zn adsorbed

$$= 100 \text{ X} \left\{ \frac{Zn_{ex}\, \rho\, (1-n)}{Zn_{ex}\, \rho\, (1-n) + (0.001)\, [Zn_{max}]\, n} \right\}, \qquad (3)$$

where 0.001 is a conversion factor (from liters to cubic centimeters); a porosity (n) of 0.4 and solid-phase density (ρ) of 2.65 g/cm^3 were assumed.

The results of a small-scale tracer test performed at the Mixed site provide further corroboration for the presence of adsorbed Zn associated with the peak in the Zn concentration profile. The tracer cloud was injected into the depth range shown in figure 4C, but immediately spread up and down 0.25 m, which is equivalent to one sampling port on the MLS. The tracer cloud contained an excess of free EDTA. The upper part of the tracer cloud intercepted the peak in the dissolved Zn profile; the lower part of the tracer cloud traveled through the region below the peak where there was no dissolved Zn. Breakthrough curves for Zn and Br, 4 m downgradient from the injection MLS for the lower part of the tracer cloud, showed conservative movement of both Zn and Br (fig. 6B). In contrast, breakthrough curves for the upper part of the tracer cloud showed an increase in the relative concentration of Zn (fig. 6A), indicating that the excess EDTA leached adsorbed Zn from the aquifer material in the upper part of the tracer cloud. Breakthrough curves for the upper and lower regions of the tracer cloud 22 m downgradient from the injection MLS showed the same relationship between Zn and Br. Experimental studies have shown that Zn-EDTA complexes do not adsorb on CCAM near pH 6 (Davis, Kent, Rea, Maest, and Garabedian, 1991). Lack of adsorption of Zn-EDTA complexes in the tracer test resulted in the absence of retardation of Zn relative to Br that is evident in the breakthrough curves (fig. 6).

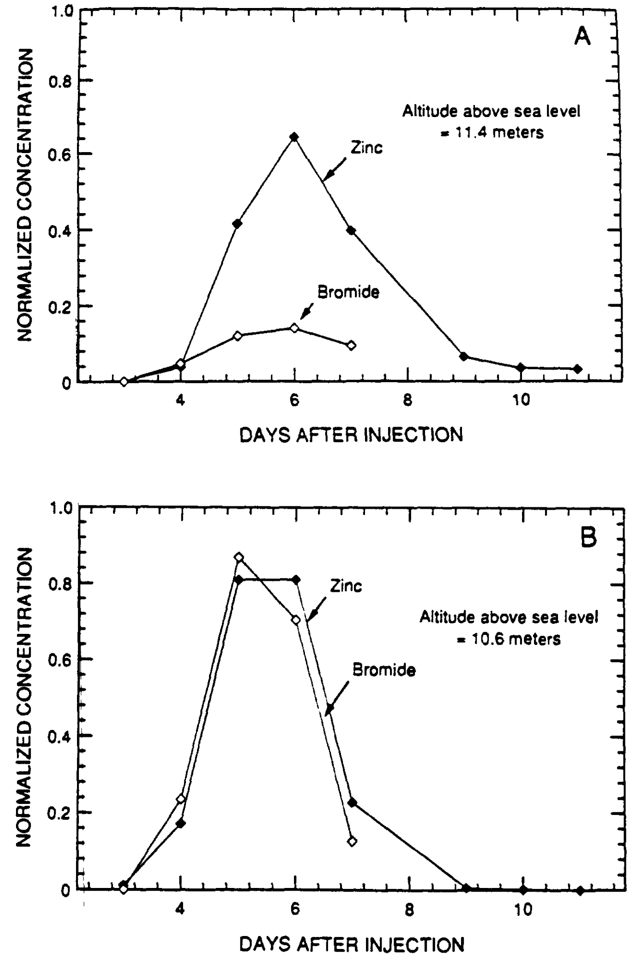


Figure 6. Breakthrough curves 4 meters from the injection multilevel sampling devise (MLS) at Mixed site. (A) Breakthrough curves from the upper part of the tracer cloud. (B) Breakthrough curves from the lower part of the tracer cloud.

Zn is known to be a constituent of domestic and industrial wastewaters (Foerstner and Van Lierde, 1983). In domestic sewage, Zn is derived primarily from corrosion of pipes. We have not yet been able to locate historical data on Zn content of the sewage effluent from the Otis Air Base treatment facility. The effluent was sampled in 1989 and 1990, but the data were not available for inclusion in this report.

Zn contamination in the transition zone was detected at the Suboxic site but was not detected 60 m downgradient at MLS in row 52 (R52 in fig. 1). A sampling program was implemented in the summer of 1990 to improve the accuracy of the location of the leading edge of the Zn plume in the transition zone, but the data were not yet available.

Comparison of the extent of the Zn plume with that of the sewage plume underscores the extent of retardation of Zn in the transition zone. The leading edge of the Zn plume in the transition zone is approximately 350 m downgradient from S318, located in the disposal beds (fig. 1). A retardation factor (R_f) on the order of 10 is obtained if the leading edge of the sewage plume is assumed to be 4 km downgradient from the source. Retardation factors for Zn can also be estimated from the predicted fractional Zn adsorption in the aquifer (dashed curve, fig. 3) by the equation

$$R_f = 1 + \frac{1-n}{n} \rho \frac{(f_{Zn})}{1 - f_{Zn}}, \qquad (4)$$

where f_{Zn} is the fraction of Zn adsorbed at a given pH. Equation 4 yields retardation factors of approximately 10 and 100 at pH values of 5 and 6, respectively. Above pH 6, the computed R_f approaches infinity as f_{Zn} approaches 1. Thus, retardation factors estimated from adsorption behavior and travel distances are in qualitative agreement.

The absence of dissolved and adsorbed Zn in the plume below the transition zone indicates that some process or processes act to immobilize Zn near the sewage-infiltration beds below the transition zone. Research targeted at identifying the immobilization process is underway; preliminary results indicate that adsorption onto the aquifer material is the immobilization process. Figure 7A shows profiles of pH and dissolved Zn from a MLS in one of the infiltration beds (S318 M1 in fig. 1). Below the top two depths, the pH is constant at 5.9 ± 0.1, reflecting the fact that sewage effluent is buffered at a pH value near 6. Elevated concentrations of dissolved Zn occur only at the uppermost sampling port,

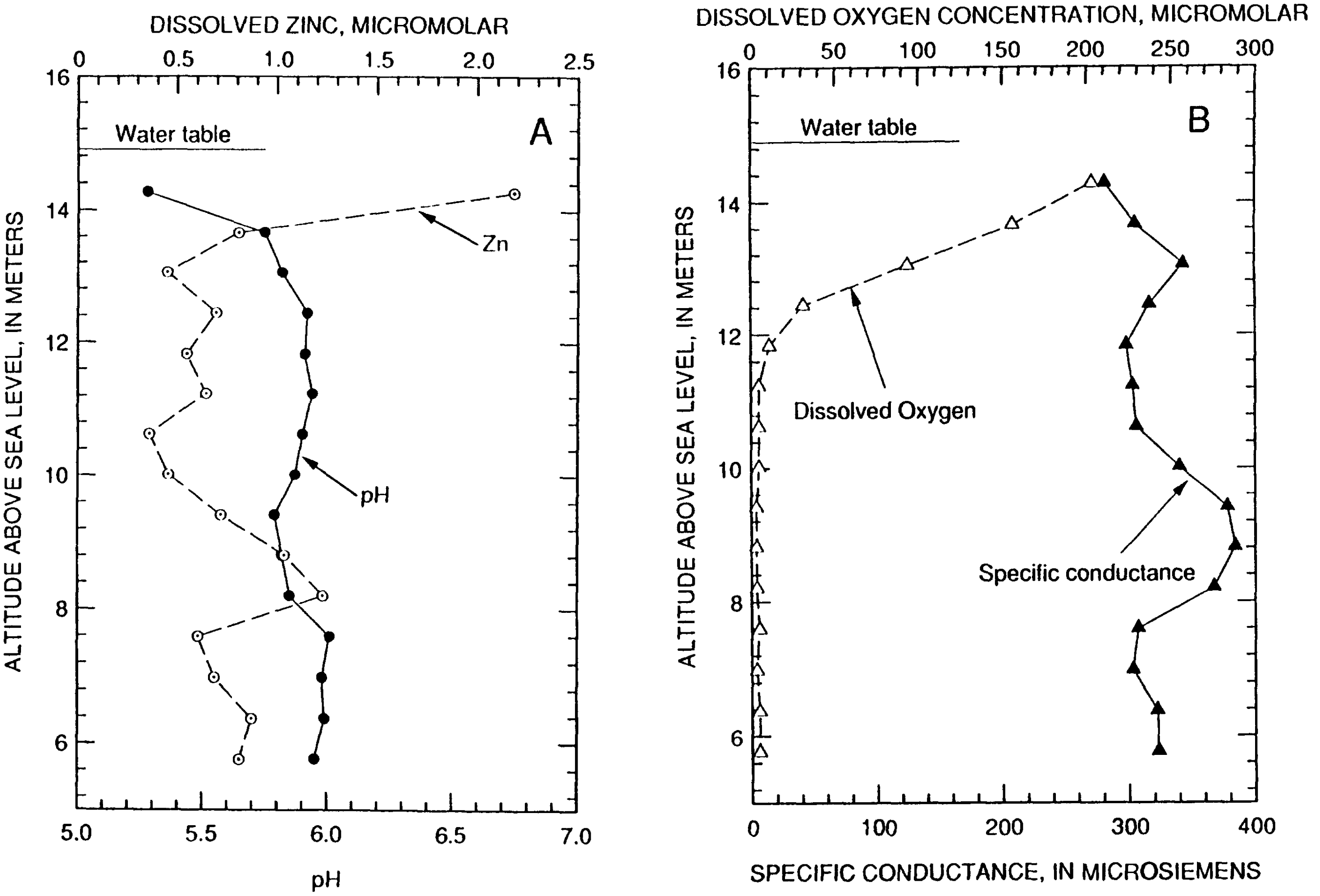


Figure 7. Vertical profiles of ground-water chemistry in one of the sewage-disposal beds (S318 M1). (A) pH and dissolved zinc as a function of depth. (B) Dissolved oxygen concentration (open triangles) and specific conductance at 20 degrees Celsius (closed triangles) as a function of depth.

which has the lowest pH value. Figure 7B shows profiles of dissolved oxygen concentration and specific conductance. These data are in excellent agreement with previous determinations at this site (Smith and others, 1991). Concentrations of dissolved sulfide and Fe(II) were below the detection limit throughout the depth range shown in figure 7, indicating that conditions are not sufficiently reducing for sulfide production to occur. Therefore, it is unlikely that precipitation of ZnS is the immobilization process.

Immobilization of Zn by adsorption in the sewage-contaminated zone could occur as follows. Predicted Zn adsorption in the aquifer (dashed curve in fig. 3) suggests that the retardation factor approaches infinity as f_{Zn} approaches 1; hence, Zn should be immobilized by adsorption at pH values above 6. The pH values in the sewage-contaminated zone increase downgradient from the disposal beds, probably because of the consumption of acid associated with microbial metabolic processes. Therefore, the retardation factor increases towards infinity with distance downgradient in the sewage plume. On the other hand, some extremely slow migration of Zn could occur in the sewage-contaminated zone despite the extensive adsorption predicted in figure 3. The concentration of surface sites on constituents of the aquifer material is fixed but the supply of Zn is continuous. Eventually, all surface sites will become occupied by Zn or other metal ions. Therefore, limited migration can occur once saturation of surface sites has occurred.

In contrast, conditions in the transition zone allow transport of Zn to occur. The ground water just below the water table consists of sewage effluent that has entrained sufficient oxygen and acid from the unsaturated zone and pristine recharge water to counteract its oxygen demand and buffer capacity (fig. 7). Just below the water table, the pH is about 5.3. At pH 5.3, the predicted f_{Zn} is about 0.9 (fig. 3), which corresponds to a retardation factor of approximately 37. Downgradient from the infiltration beds, the pH at the top of the plume decreases because of interaction of the plume with recharge water, which has pH values below 5.0 (Davis, Kent, Rea, Maest, and Garabedian, 1991). Thus, the retardation factor in the transition zone decreases downgradient from the disposal beds. Only in the transition zone are the pH values low enough to allow Zn to be mobile in the presence of excess adsorption sites on the aquifer material. Even at these low pH values, however, adsorption of Zn onto the aquifer material is extensive, which greatly retards the transport of Zn.

The immobilization of Zn at or near the disposal beds in the sewage plume has an important consequence. A potentially large reservoir of Zn has accumulated on the aquifer material as a result of the immobilization process. Other adsorbing metal ions contained in the effluent would also be expected to accumulate. A subsequent change in aquifer chemistry could lead to remobilization of Zn and the other metals in this zone. One such example was provided by the tracer test in which adsorbed Zn was mobilized by adding EDTA (fig 6A). A second example would be the cessation of disposal of treated sewage, which would lead to a gradual decrease in pH in the aquifer, because the recharge water has a lower pH than the sewage effluent. If the Zn immobilization process is adsorption onto the aquifer material as proposed above, Zn would be released by desorption in response to the decrease in pH (fig. 3). This would lead to a pulse of Zn-contaminated water that would migrate slowly because of significant retardation. Other adsorbed metals may also be released or many remain immobilized, depending on their adsorptive and other chemical properties.

SUMMARY

Disposal of effluent from the Otis Air Base sewage-treatment facility into the sand and gravel aquifer on Cape Cod, Mass., has resulted in contamination of the aquifer with Zn. At sites up to 350 m downgradient from the disposal site, a zone of dissolved Zn is supported by a reservoir of adsorbed Zn. The contamination is limited to a 1- to 2-m thick zone at the upper margin of the sewage plume. At greater depths, the sewage plume is devoid of Zn, indicating that processes upgradient have led to immobilization of Zn. Preliminary evidence supports the hypothesis that adsorption onto the aquifer material, which is nearly complete at pH values characteristic of the sewage-contaminated zone, is the process responsible for immobilization. If true, a large reservoir of immobilized Zn is in the vicinity of the disposal bed that could be mobilized by future changes in the aquifer chemistry. Cessation of disposal of sewage effluent would lead to a decrease in pH and, hence, to mobilization of some of the adsorbed Zn. Addition of the strong complexing agent EDTA also has mobilized adsorbed Zn.

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BACKGROUND AQUEOUS CHEMISTRY OF SHALLOW GROUND WATER IN A SEWAGE-CONTAMINATED GLACIAL OUTWASH AQUIFER, CAPE COD, MASSACHUSETTS

By Roger W. Lee[1]

ABSTRACT

Chemical data were collected in 1988-89 from 36 wells representing 18 uncontaminated sites in the vicinity of a sewage plume emanating from disposal areas at Otis Air Base. These samples had low concentrations of dissolved solids (generally less than 150 milligrams per liter); pH, and concentrations of dissolved solids and silica generally increased with depth in the aquifer. Although road-salting practices appear to have added solutes to shallow ground water at a few locations, this practice did not affect ground water at three sites where concentrations of dissolved solids decrease with increasing depth. A geochemical model using the computer code PHREEQE matches observed chemical data with chemical reactions that involve incongruent dissolution of feldspar minerals to kaolinite, and dissolved CO_2 in recharge water, that varies from about 0.05 to 0.4 millimoles per liter. This result suggests that a nonuniform distribution of CO_2 may exist in the unsaturated zone in the study area. The various land-use practices and surface features, such as residential subdivisions, golf courses, large cultivated grass fields, kettle ponds, and conifer forests, each may cause variations in the production of CO_2 or in the flux of CO_2 from the unsaturated zone into the water table aquifer.

INTRODUCTION

Recent research in ground water at the U.S. Geological Survey Cape Cod Toxic-Substances Hydrology site near Falmouth, Mass., has focused on hydrological, geochemical, and microbiological processes in and around a sewage plume present in the glacial outwash aquifer. The research ultimately will focus on sediment-water chemical interactions in the vicinity of the plume. The initial phase of the research, however, deals with the chemistry of water in the aquifer without the effects of the sewage effluent. The purpose of this paper is to identify the mineral-water interactions occurring within the unaffected part of the shallow water-table aquifer.

Water-chemical data from 36 wells at 18 sites adjacent to the contaminant plume were studied (fig. 1). Data from water samples collected in 1988-89 were compiled and analyzed using the geochemical model WATEQF (Plummer and others, 1976). A reaction model was developed using the computer code PHREEQE (Parkhurst and others, 1980) to test the hypothesized chemical evolution of shallow ground water against actual chemical data.

HYDROGEOLOGY

The water-table aquifer consists of glacial outwash sand and gravel that overlies a thick glacial till of silty sand and clay (Oldale, 1969). The outwash ranges from about 90 to 200 ft (feet) thick, averaging about 150 ft thick (Garabedian and LeBlanc, 1991, this Proceedings, fig. 2). The area of interest (fig. 1) extends from the southern part of Otis Air Base to as far south as the cranberry bogs. Ground water flows generally north to south in this area (fig. 1). Sewage effluent has been discharged to sand infiltration beds on the southern edge of Otis Air Base since about 1949, and has followed this flow direction to the current (1990) position of the plume.

AQUIFER CHEMISTRY

Geochemical mass transfer in ground water is determined by aquifer mineralogy, chemistry of the pore water, and equilibrium analyses of the pore water chemistry. Knowledge and understanding of these phenomena provide insight necessary to development of conceptual and quantitative models of the geochemical processes occurring within an aquifer.

Mineralogy

Minerals comprising the glacial outwash sands and gravels have been previously described (Wood and others, 1990). The sediments are well-sorted fine- to medium-grained sand with interspersed gravel to cobble zones. The sands contain principally quartz with small amounts of feldspar (albite, orthoclase, and microcline). Clay minerals are extremely 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, or organic coatings on gravels and sand grains.

Water Chemistry

Water chemistry and the distribution of solutes associated with the sewage plume have been described previously (LeBlanc, 1984). Data collected during the summer of 1988 to the summer of 1989 to determine background water chemistry are given in table 1. Background waters are dilute and generally contain less than 150 mg/L (milligrams per liter) dissolved solids. Hydrochemical facies vary from no dominant cations or anions to sodium-bicarbonate or sodium-chloride dominated water. Waters that contain relatively high concentrations of dissolved solids (greater than 150 mg/L) and dominated by sodium chloride ions indicate possible surface contamination from winter road-salting practices (D.R. LeBlanc, U.S. Geological Survey, oral commun., 1988).

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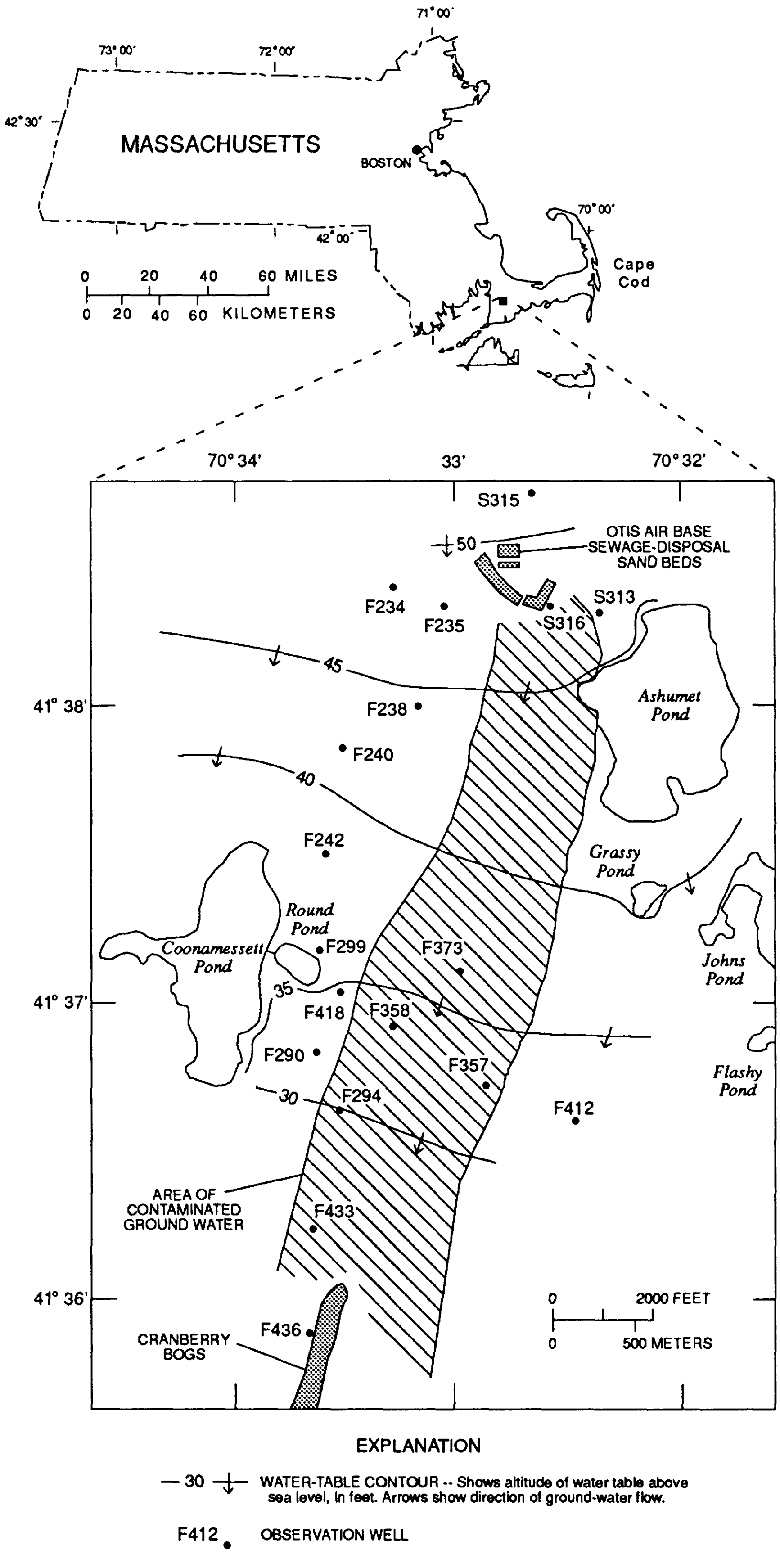
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33'
70°32'
S315
50
OTIS AIR BASE SEWAGE-DISPOSAL SAND BEDS
F234
F235
S313
S316
45
41° 38'
F238
Ashumet Pond
F240
40
F242
Grassy Pond
Round Pond
Coonamessett Pond
F299
F373
Johns Pond
41° 37'
35
F418
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F357
Flashy Pond
30
F294
F412
AREA OF CONTAMINATED GROUND WATER
F433
41° 36'
0 2000 FEET
0 500 METERS
CRANBERRY BOGS
F436
EXPLANATION
30 WATER-TABLE CONTOUR -- Shows altitude of water table above sea level, in feet. Arrows show direction of ground-water flow.
F412 OBSERVATION WELL

Figure 1. Water table map and location of background water samples for the area of investigation (LeBlanc, 1984).

Table 1. *Well numbers, depth, water-chemical data, and means of chemical data for background water samples from the Cape Cod site*

[Chemical data are in milligrams per liter unless otherwise specified]

Well number	Depth (feet)	Temperature (°C)	pH (units)	Calculated dissolved solids	Ca	Mg	Na	K	HCO_3	SO_4	Cl	NO_3	SiO_2	Dissolved O_2	Total CO_2 (millimoles per liter)
S313.038	38	9.0	5.70	37	0.93	0.89	9.30	0.80	2.51	5.7	10.0	2.08	6.20	11.2	0.273
S313.060	60	10.0	5.60	65	2.40	3.00	12.00	1.60	2.17	21.0	12.0	3.54	8.70	10.6	.286
S313.080	80	10.0	5.90	46	2.60	2.30	6.30	.80	2.29	15.0	6.8	2.44	9.50	11.4	.171
S315.149	149	13.0	6.08	61	2.17	1.10	7.94	.52	11.98	7.7	12.0	1.42	11.19	11.0	.629
S316.082	82	11.0	6.50	138	27.00	7.10	14.00	5.30	25.79	22.0	37.0	1.82	12.00	.8	.783
S316.134	134	11.0	6.50	63	3.90	2.80	6.70	4.40	7.22	16.0	8.6	5.76	12.00	1.8	.221
F234.099	99	10.0	5.70	64	3.90	2.80	9.60	1.40	4.13	17.0	11.0	5.76	11.00	10.3	.446
F235.094	94	10.5	5.60	65	4.20	1.90	7.20	1.60	2.37	25.0	12.0	3.37	9.20	9.0	.309
F238.106	106	10.0	5.70	69	4.50	4.10	8.20	.90	2.94	27.0	9.8	3.99	9.80	9.4	.316
F240.095	95	9.5	5.80	35	1.50	1.80	5.80	.50	3.26	5.4	10.0	.71	8.30	10.8	.296
F242.077	77	10.0	5.80	38	1.50	1.90	6.30	.60	4.82	7.3	9.2	.44	8.60	10.7	.432
F290.091	91	10.0	6.20	60	4.40	2.00	8.50	.80	7.55	6.8	9.0	13.70	12.00	1.4	.343
F294.064	64	10.0	5.80	56	1.40	1.80	15.00	.70	1.48	4.8	24.0	.01	7.90	10.8	.132
F294.109	109	9.5	6.30	75	8.80	4.30	14.00	1.10	17.31	4.9	14.0	.44	19.00	2.0	.685
F299.020	20	9.0	5.40	59	7.70	1.80	5.40	1.10	2.01	9.1	9.0	17.20	6.90	9.5	.409
F357.079	79	9.5	5.60	62	1.80	3.20	13.00	.90	2.91	13.0	16.0	4.87	8.30	10.2	.387
F357.099	99	12.2	5.60	44	1.79	2.06	6.85	.60	9.99	5.3	11.2	3.30	8.73	9.7	1.270
F358.049	49	10.5	5.50	25	1.10	.85	4.00	.90	.54	4.3	7.8	.00	6.00	12.2	.088
F358.089	89	9.5	6.00	33	1.20	.96	5.70	.50	2.57	5.8	7.0	1.82	9.00	5.4	.163
F373.060	60	13.0	5.68	53	1.75	1.66	10.50	.68	5.99	6.5	14.6	5.75	8.99	8.2	.640
F373.113	113	12.2	6.31	99	8.82	3.36	15.30	1.42	40.65	6.0	16.2	9.29	19.47	.1	1.530
F412.042	42	10.0	5.50	28	0.66	1.20	4.40	.50	.63	6.0	9.3	.00	5.90	11.2	.100
F412.064	64	9.5	5.80	81	0.54	1.00	25.00	.90	1.44	19.0	27.0	.53	6.60	11.1	.130
F412.078	78	9.5	5.50	169	3.30	4.50	52.00	1.70	.36	5.3	94.0	1.86	6.80	9.0	.057
F412.091	91	9.5	5.50	182	4.40	5.90	54.00	2.10	1.49	7.4	100.0	.00	7.50	6.4	.240
F412.108	108	9.5	5.70	119	3.20	3.50	34.00	.90	2.80	7.1	60.0	2.30	7.30	6.0	.300
F418.089	89	9.5	5.80	54	3.70	3.20	7.20	.80	1.69	4.6	16.0	8.86	9.20	4.8	.150
F418.103	103	9.5	6.20	72	6.70	3.00	10.00	1.00	5.75	5.9	21.0	10.60	11.00	5.7	.260
F418.122	122	9.5	6.40	65	5.10	2.30	9.70	1.20	11.39	7.2	9.7	6.64	18.00	2.0	.400
F418.141	141	9.5	6.40	63	4.40	2.10	9.30	1.00	9.84	6.1	9.4	10.10	16.00	3.9	.340
F433.064	64	9.0	5.50	44	1.40	1.80	8.80	.90	1.58	7.0	13.0	4.03	6.70	9.7	.260
F433.090	90	9.0	5.90	71	2.60	2.40	17.00	1.30	6.15	9.0	23.0	3.94	9.10	9.6	.460
F433.104	104	9.5	6.30	78	5.50	2.40	16.00	1.50	13.06	10.0	12.0	8.41	16.00	.5	.520
F436.036	36	10.0	5.60	31	.88	1.20	5.80	1.00	1.26	6.0	9.6	.00	6.30	8.8	.170
F436.060	60	13.0	5.76	54	2.70	1.81	10.70	.71	6.99	4.5	19.5	1.50	9.22	11.0	.640
F436.076	76	9.0	6.70	80	12.00	2.90	10.00	1.70	24.27	13.0	12.0	2.39	15.00	0.2	.620
Mean			5.88	68	4.22	2.52	12.93	1.23	6.92	9.8	19.2	4.14	10.09	7.4	.400

If a homogeneous mineral assemblage and uniform recharge chemistry are assumed, then the chemical samples collected at increasing depths in the aquifer at a given site would be expected to show a proportionately increasing degree of reaction and chemical evolution of water resulting from increased contact time with the aquifer matrix. Concentrations of dissolved silica increase with depth (fig. 2) as do values of pH (fig. 3). Figure 4, however, shows that concentrations of dissolved solids decrease with increasing depth at well sites S313, F412, and F418, implying less mineral dissolution along flow paths to some deeper wells.

Dissolved oxygen was present in ground water in nearly all samples analyzed. Therefore, oxidation of organic matter or other reduced substances in the aquifer probably is not a significant chemical process. Reducing environments may be present in deep parts of the aquifer associated with the till layer as indicated by water samples from deep wells at F436 (K.M. Hess, and D.R. LeBlanc, U.S. Geological Survey, written commun., 1989).

Equilibrium Analyses

Equilibrium analyses of the chemical data using WATEQF show undersaturation of most common mineral phases, including feldspars, and saturation to supersaturation of quartz and kaolinite. All data plot in the kaolinite stability

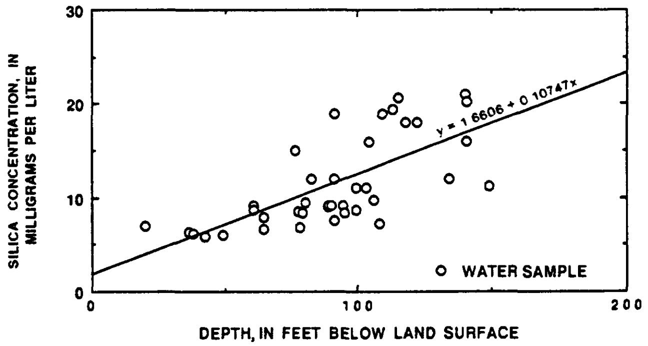

Figure 2. Variation of silica with depth and least-squares line fit of data for background water samples from the study area.

field on an activity-activity diagram (fig. 5). Incongruent dissolution of feldspars to kaolinite is a reaction consistent with these results:

$$\underset{\text{(albite)}}{2NaAlSi_3O_8} + 2CO_2 + 11H_2O \Rightarrow \underset{\text{(kaolinite)}}{Al_2Si_2O_5(OH)_4} + 2Na^+ + 2HCO_3^- + 4H_4SiO_4. \qquad (1)$$

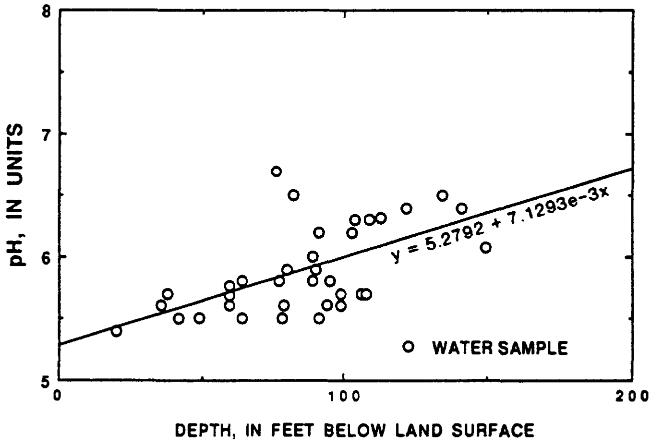

Figure 3. Variation of pH with depth and least-squares line fit of data for background water samples from the study area.

REACTION MODEL

On the basis of observed chemical data, aquifer mineralogy, and chemical composition of rainfall, it is possible to construct a reaction sequence for background chemical evolution of water in the glacial sand and gravel aquifer. A generalized reaction model is shown in figure 6.

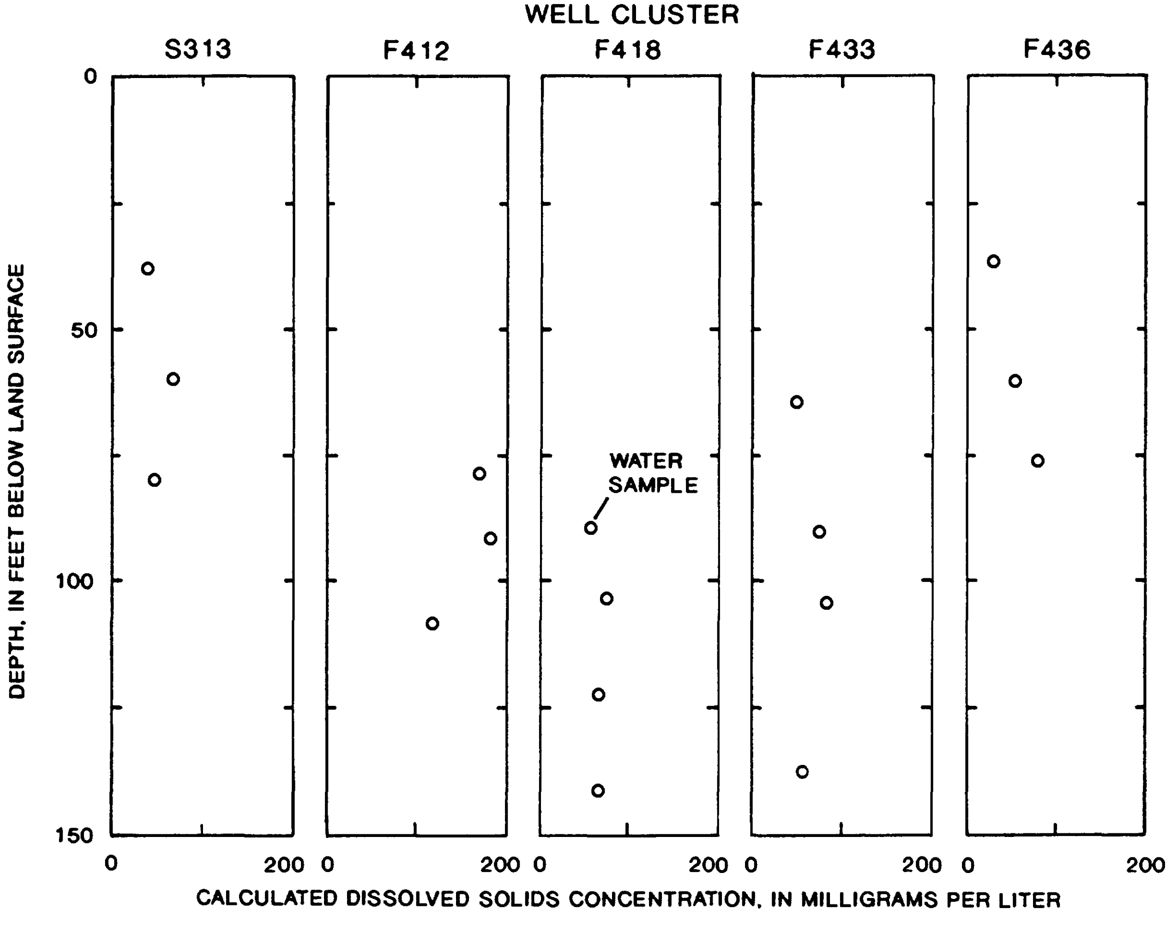

Figure 4. Variation of concentrations of dissolved solids with depth in the aquifer at selected well clusters in the study area.

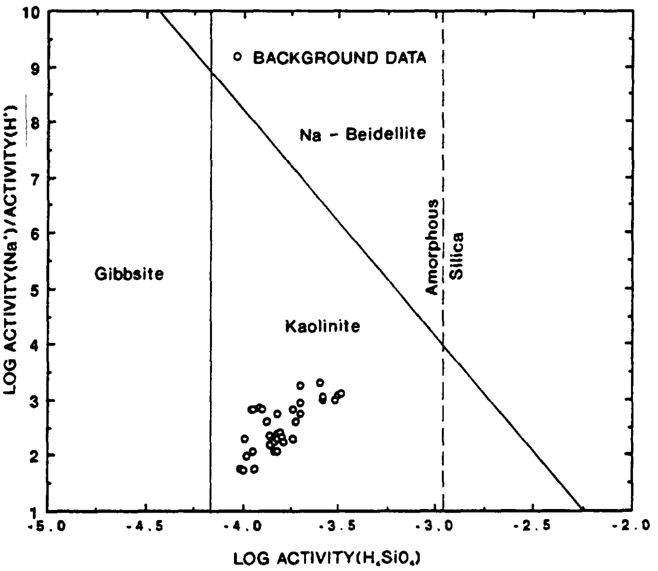

Figure 5. Stability relations in the system Na_2O-Al_2O_3-SiO_2-H_2O at 10 degrees Celsius and water samples from the study.

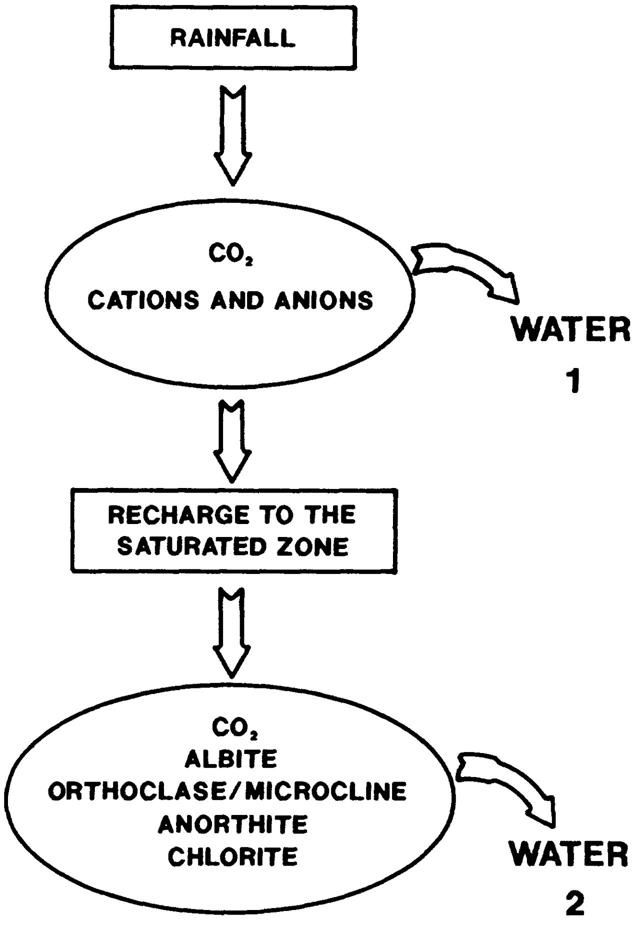

Figure 6. General reaction model for water in the glacial sand and gravel aquifer.

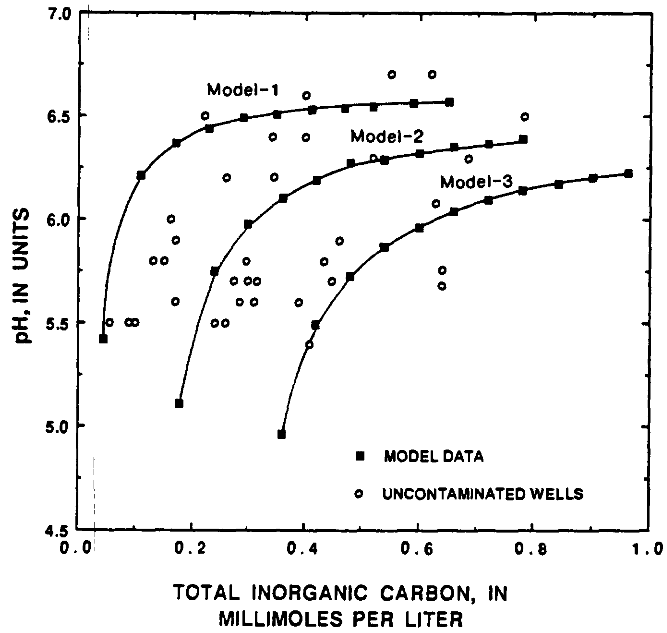

Figure 7. Comparison of pH with total inorganic carbon for PHREEQE model results of chemical evolution and data from water samples in the study area.

The magnitude of reaction processes producing water 1 determines the chemistry of water 2. The magnitude 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).

Significant vertical variations of chemical constituents imply one or more components of inhomogeneity in the chemical system. This complicates development of a single quantitative mass-transfer model. The modeling process is further complicated by the nearly impossible task of collecting chemical data along flow paths in a water-table aquifer for comparison of the model result to chemical data.

The reaction model proposed in figure 6 was tested against actual chemical data using the computer code PHREEQE (Parkhurst and others, 1980). Results and modeling steps are given in table 2. It was necessary to develop models with varying amounts of CO_2 available for the feldspar hydrolysis reactions to match more closely most of the background observed chemical data for solutes, pH, and CO_2. Three models were developed that cover most of the observed range of concentrations of solutes; they show chemical evolution of pH and total inorganic carbon for variable CO_2 input ranging from about 0.05 to 0.4 mmol/L (millimoles per liter) at recharge (fig. 7). With some exceptions, the data agree with the models: CO_2 controlled feldspar hydrolysis to kaolinite.

Variations of input in chemical data are probably attributable to nonuniform distributions of CO_2 input to ground water over the study area. This condition may occur because of thin soil cover over the quartz sands, effects of local variation in land cover such as conifer forests, influence of kettle ponds, and cultural features such as suburban development, golf courses, and the vast, cleared areas of Otis Air Base. Variation in land cover have been shown to affect water chemistry in the unsaturated zone in a similar geohydrologic setting (Moss, 1990). The surficial features in the study area may affect CO_2 production in the unsaturated zone or may influence the flux of water and CO_2 through the unsaturated zone.

Table 2. *PHREEQE mass transfer simulations*

[Concentrations in millimoles per liter unless otherwise specified]

		Recharge water	
	Model 1	Model 2	Model 3
CO_2	0.045	0.182	0.364
pH (units)	5.42	5.11	4.96
Ca	.036	.036	.036
Mg	.036	.036	.036
Na	.205	.205	.205
K	.011	.011	.011
Cl	.216	.216	.216
SO_4	.072	.072	.072
NO_3	.004	.004	.004

Add minerals to above solution in 10 steps
0.025 NaCl (halite)
.200 $NaAlSi_3O_8$ (albite)
.025 $KAlSi_3O_8$ (orthoclase)
.050 $CaAl_2Si_2O_8$ (anorthite)
.005 $Mg_5Al_2Si_3O_{10}$ (chlorite)
.600 CO_2(gas)
Subtract (precipitate) mineral from solution at each step
0.162 $Al_2Si_2O_5(OH)_4$ (kaolinite) total subtracted in step 10

		Final solution	
	Model 1	Model 2	Model 3
CO_2	0.645	0.782	0.964
pH (units)	6.57	6.39	6.23
Ca	.086	.086	.086
Mg	.061	.061	.061
Na	.430	.430	.430
K	.036	.036	.036
Cl	.241	.241	.241
SO_4	.072	.072	.072
NO_3	.004	.004	.004
SiO_2	.455	.455	.455

CONCLUSIONS

Background ground water at the Cape Cod research site contains low concentrations of dissolved solids (less than 150 mg/L), and variable concentrations of solutes. The principal chemical process is hypothesized to be incongruent dissolution of feldspars, mostly albite, with the formation of kaolinite. Cations that increase in the aqueous phase are predominantly sodium and bicarbonate, but silica increases to as much as 19 mg/L. Increasing depth in the aquifer does not always correlate with increasing concentrations of dissolved solids as might be expected for a relatively homogeneous chemical system. PHREEQE mass-transfer modeling, based principally on incongruent feldspar dissolution, demonstrates that variable CO_2 uptake by recharge water in the unsaturated zone is one process that may account for most of the differences in background ground-water chemistry observed in the glacial outwash aquifer. The amount of CO_2 in the unsaturated zone appears to vary from 0.05 to 0.4 mmol/L in recharge water in the study area. It is likely that effects of land-surface cover, such as residential subdivisions, golf courses, and the open, grassy areas of Otis Air Base and elsewhere in the oak and conifer forests, could affect the production of CO_2 and its flux from the unsaturated zone into the aquifer.

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BIOGEOCHEMICAL FATE OF ORGANIC COMPOUNDS IN SEWAGE-CONTAMINATED GROUND WATER, CAPE COD, MASSACHUSETTS

By Larry B. Barber, II[1], E. Michael Thurman[2], Jennifer A. Field[3], Jerry A. Leenheer[1], *and* Denis R. LeBlanc[4]

ABSTRACT

The past 11 years of research on the occurrence and distribution of organic and inorganic compounds in a ground-water contamination plume at the Cape Cod Toxic-Substances Hydrology Research site near Falmouth, Massachusetts, have provided insight into the biogeochemical processes controlling their fate and transport in ground water. The plume of organic contaminants, a result of disposal of secondary-sewage effluent into a sand and gravel aquifer, has a very complex composition and is migrating from the rapid infiltration beds at about 300 feet per year. A hierarchical analytical approach was used to determine the predominant organic compounds present. The major organic contaminants fall into two classes: volatile chlorinated hydrocarbons, and surfactant-derived products. The volatile chlorinated hydrocarbons, which include di-, tri-, and tetrachloroethene, do not appear to undergo biodegradation or sorption to the aquifer sediments. On the other hand, anionic and nonionic surfactants undergo biodegradation and sorption to the aquifer sediments.

INTRODUCTION

A plume of contaminants in ground water at the Cape Cod Toxic-Substances Hydrology Research site near Falmouth, Mass., has been extensively studied since 1978; details of compound distributions and processes controlling the fate of organic contaminants in the plume have been published by Barber and others (1984), Barber (1985), Thurman and others (1986), Thurman and others (1987), Barber (1988), Barber and others (1988), Field (1990), and Field and others (in press). The plume of contamination results from discharge of secondary-treated sewage effluent into sand-infiltration beds and subsequent percolation into a highly permeable, sand and gravel aquifer (LeBlanc, 1984). Figure 1 shows the location of the site and the generalized extent of contamination. This paper presents a brief overview of the biogeochemical fate of organic contaminants in the plume.

METHODS

Ground-Water Sampling

Ground-water samples were collected from observation wells at the site during 1978, 1979, 1983, 1985, and 1988. The wells are constructed of 1.25- to 2.0-inch polyvinyl chloride with short screens (typically 2 feet long); most wells are in clusters and are screened at different depths. A full range of organic and inorganic analyses were performed on each sample. Samples were collected using a peristaltic or a submersible pump, fitted with Teflon[5] discharge lines, and were handled and preserved by standard procedures as described by Barber (1985).

Analytical Methods

The field investigation involved the development of a hierarchical analytical approach for determining the wide range of organic compound types and quantities present in the contaminated ground water. The hierarchical approach involves a series of analyses that increase in compound selectivity and sensitivity.

First, the extent of contamination was defined on the basis of inorganic chemicals and properties such as specific conductance and concentrations of chloride and boron. After the boundaries of the plume were defined, organic compounds in the ground water were characterized by: (1) bulk analyses (concentrations of total organic carbon, dissolved organic carbon, and purgeable organic carbon), (2) class-specific analyses (dissolved organic carbon fractionation, and concentrations of methylene-blue-active substances and total purgeable organic chlorine), and (3) compound-specific analysis (closed-loop stripping, purge and trap, liquid-liquid extraction, and solid-phase extraction followed by gas chromatography/mass spectrometry (GC/MS) or high performance liquid chromatography/fluorescence detection (HPLC/FD) analysis). Bulk and compound-class specific analysis was carried out on solid-phase-extraction isolates obtained from large-volume water samples using infrared spectroscopy, proton nuclear magnetic resonance spectrometry, and carbon-13 nuclear magnetic resonance spectrometry.

COMPOUND OCCURRENCE AND DISTRIBUTION

The overall plume of contamination, as defined by specific conductance, and concentrations of chloride and boron, extends more than 3,500 m (meters) downgradient from the infiltration beds, is more than 1,000 m wide, and is more than 30 m thick. The plume of dissolved organic carbon contamination has similar dimensions as the plume of inorganic constituents, but highest concentrations are found in the area immediately adjacent to the infiltration beds and in the downgradient one-third of the plume (Thurman and others, 1986). Dissolved organic carbon fractionation analysis indicates that the compositions of the

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[1] U.S. Geological Survey, Denver, Colo.

[2] U.S. Geological Survey, Lawrence, Kans.

[3] Swiss Federal Institute for Water Resources and Water Pollution Control, Dubendorf, Switzerland

[4] U.S. Geological Survey, Marlborough, Mass.

[5] The use of brand, firm, or trade names used in this paper is for identification purposes only and does not imply endorsement by the U.S. Geological Survey.

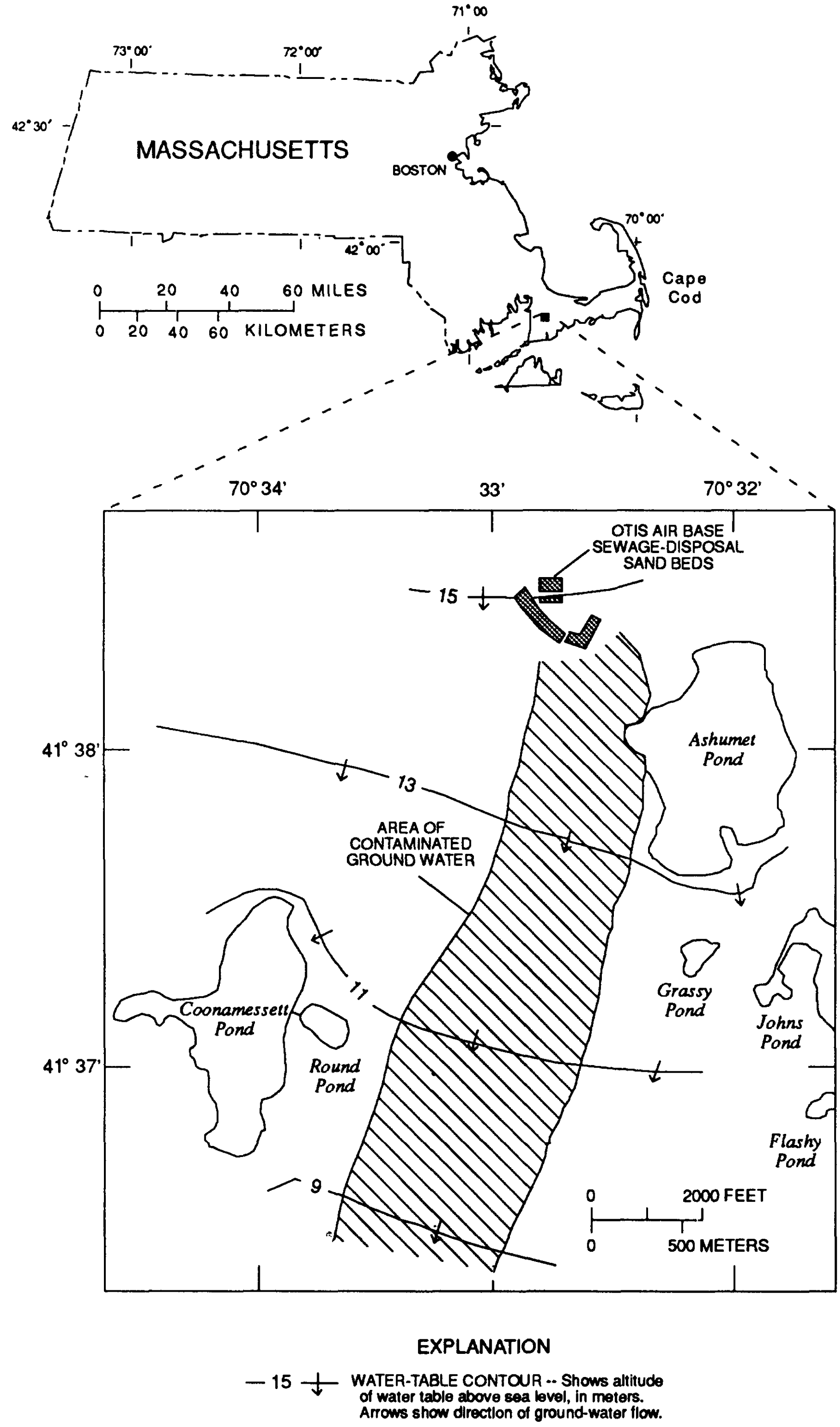
71°00
73°00'
72°00'
42°30'
MASSACHUSETTS
BOSTON
70°00'
42°00'
Cape Cod
0 20 40 60 MILES
0 20 40 60 KILOMETERS
70°34'
33'
70°32'
OTIS AIR BASE SEWAGE-DISPOSAL SAND BEDS
15
Ashumet Pond
41° 38'
13
AREA OF CONTAMINATED GROUND WATER
11
Grassy Pond
Johns Pond
Coonamessett Pond
Round Pond
41° 37'
Flashy Pond
9
0 2000 FEET
0 500 METERS
EXPLANATION
15
WATER-TABLE CONTOUR -- Shows altitude of water table above sea level, in meters. Arrows show direction of ground-water flow.

Figure 1. Study area location map showing generalized outline of the contamination plume.

two zones of elevated dissolved organic carbon concentrations are dissimilar (Barber, 1985)--the zone near the infiltration beds consists of nearly equal amounts of hydrophobic and hydrophilic compounds, whereas the downgradient zone consists predominantly of hydrophobic-neutral compounds. The zone of hydrophobic-neutral dissolved organic carbon coincides with the zone of maximum methylene-blue-active substances. Methylene-blue-active substances analysis measures anionic surfactants, such as linear- and branched- chain alkylbenzenesulfonates. The presence of linear- and branched-chain alkylbenzenesulfonates was confirmed using HPLC/FD, derivitization GC/MS, and carbon-13 nuclear magnetic resonance spectrometry of isolates obtained by solid-phase extraction. Results of using the derivitization method (to form the trifluoroethyl esters of the benzenesulfonic acid) indicate that the anionic-surfactant component of the contaminated ground water is very complex and consists of the parent compounds, synthesis impurities such as dialkyltetralinsulfonates, and sulfophenylcarboxylate degradation products (Thurman and others, 1987; Field, 1990; Field and others, in press). The degradation products of alkylphenol-polyethoxylate nonionic surfactants (APEO) were detected by liquid-liquid-extraction, solid-phase-extraction, and closed-loop-stripping analysis.

Specific volatile and semivolatile compounds were determined by purge and trap, closed-loop-stripping, liquid-liquid-extraction, and solid-phase extraction combined with GC/MS analysis. The dominant compounds determined by purge and trap were cis- and trans-1,2-dichloroethene, trichloroethene, and tetrachloroethene. Other volatile compounds that were detected at trace concentrations include trichloromethane, tetrachloromethane, 1,1,1-trichloroethane, and 1,1-dichloroethene. Distribution of the volatile chlorinated hydrocarbons in the plume is very complex and different compounds dominate in different parts of the plume; near the leading edge of the plume, tetrachloroethene is the predominant compound; in the middle of the plume, trichloroethene predominates; and near the infiltration beds, dichloroethene predominates. The ratios of cis- and trans-1,2-dichloroethene, trichloroethene, and tetrachloroethene differ as a function of vertical position in the plume.

The closed-loop-stripping method, which is more sensitive than purge and trap and isolates a wider range of compounds, indicates that the distribution of semivolatile compounds also is very complex. In the most contaminated wells, more than 200 compounds were detected by closed-loop-stripping GC/MS, including dichlorobenzenes, aromatic and aliphatic hydrocarbons, aldehydes, ketones, alkylphenols, phthalate esters, and fatty acids (Barber and others, 1984; 1988).

The major compounds isolated by liquid-liquid-extraction are one and two ethoxy homologues of APEO surfactants, carboxylated APEO compounds, alkylphenols, and phthalate esters. The carboxylated APEO degradation products required derivitization to form the methyl esters. Several additional components were detected in the liquid-liquid-extraction extracts, but their concentrations were too low to identify and quantify.

CHANGES WITHIN THE PLUME OVER TIME

Several inorganic and organic constituents were measured during all sampling periods. Results from these analyses indicate that the plume is dynamic, and compound concentrations are changing as the contaminants move downgradient. Bulk measurements, such as specific conductance and dissolved organic carbon, changed little over time at most sites. However, these bulk measurements changed greatly in some wells along the plume boundaries as the plume advanced downgradient between 1978-88. Temporal trends for specific contaminants were considerably more variable than for bulk measurements, but also indicate movement of the plume in the downgradient direction.

BIOGEOCHEMICAL PROCESSES

Analytical results were used to define chemical zonations within the contaminant plume; these zones indicate that geochemical and biochemical processes are controlling contaminant occurrence and distribution. Although many indications of biogeochemical processes were observed, only two examples are presented here. First, the distinct zones of dichloroethene, trichloroethene, and tetrachloroethene, indicate that chemical or biological processes may be controlling their distribution. Although zonation of organic compounds can result from chromatographic separation of compounds because of sorption onto aquifer sediments, it does not appear to control the distribution of the volatile-chlorinated hydrocarbons, because their distribution is the reverse of that predicted from partition theory (Chiou and others, 1983), in that the least soluble compound has been transported the greatest distance. Biological reductive dehalogenation (Parsons and others, 1984; Parsons and Lage, 1985; Barrio-Lage and others, 1986) also could cause the observed distribution pattern, in that tetrachloroethene is converted to trichloroethene, which is converted to dichloroethene, and finally, to vinyl chloride. Alternatively, the distributions could result from changes in solvent use over time with a shift toward the less chlorinated homologues. To determine whether biodegradation or source controls the volatile-chlorinated hydrocarbon distributions, the dichloroethene isomers were evaluated. Because the reductive-dehalogenation pathway results in predominance of the cis over the trans-isomer, the isomeric ratio can be used to evaluate the relative importance of biological processes (predominantly cis). The analytical data indicate that the cis isomer is predominant, which is consistent with reductive dehalogenation.

In contrast to the behavior of the volatile-chlorinated hydrocarbons, anionic and nonionic surfactant distributions appear to be strongly affected by biological degradation and sorption. For instance, there is almost complete removal of linear alkylbenzenesulfonates, from 250 μg/L (micrograms per liter) in the sewage-effluent to less than 10 μg/L in the ground water, after 100 m of subsurface transport. However, the linear alkylbenzenesulfonates are not completely mineralized, but rather are partly degraded to their carboxylated intermediates (Field, 1990; Field and others, in press). The carboxylated biodegradation products are more soluble than the parent compound and thus are more readily transported in the ground water.

The biodegradation pathway for nonionic APEO surfactants is more complicated than it is for anionic surfactants. APEO compounds degrade to form shorter ethoxy-chain homologues, carboxylated homologues, and alkylphenols. Transport of each degradation product is different from that of the parent compound. APEO with 10 to 20 ethoxy units are the most soluble compounds, whereas the alkylphenol degradation products are the least soluble. The carboxylated degradation products are more soluble than their APEO equivalents. Because of the inverse relation between solubility and sorption, alkylphenols will be most highly retained if chromatographic separation is occurring within the aquifer, whereas the long ethoxy-chain APEO will be transported most readily. However, biodegradation during sewage treatment rapidly degrades APEO compounds to their one to three ethoxy homologues; thus, of the various metabolites, the carboxylated degradation products should be the most rapidly transported nonionic surfactant derived compounds. These predictions are consistent with the observed distributions; alkylphenols are restricted to the region near the infiltration beds; the short ethoxy-chain APEO and their carboxylated equivalents are detected in the middle of the plume; and only the carboxylated compounds are detected in the distal part of the plume.

SUMMARY

The organic geochemistry of a plume of contaminants in ground water at the Cape Cod Toxic-Substance Hydrology Research site is complex in both the types of compounds present and their distribution. A hierarchical analytical approach is required to provide information on the total mass of organic matter in the system and the nature of the compounds present. Environmental factors that control the occurrence and distribution of the organic contaminants are complex, and include sorption to the aquifer sediments, biological transformations, and changes in chemical use over time. Observed distributions of anionic and nonionic surfactants and their degradation products within the contamination plume are consistent with a coupled biological degradation/ transport model where the ease of transport is a function of the characteristics of the degradation product.

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PURGEABLE ORGANIC CHLORIDE--A SURROGATE MEASUREMENT FOR SCREENING AND MONITORING VOLATILE-CHLORINATED HYDROCARBONS IN GROUND WATER

By Larry B. Barber, II[1], E. Michael Thurman[2], Yoshi Takahashi[3], and Mary Noriega[1]

ABSTRACT

A combined field and laboratory study was conducted that compared results from purge and trap gas chromatography/mass spectrometry (PT-GC/MS) and purgeable organic chloride (POCl) analysis for measuring volatile chlorinated hydrocarbons (VCH) in water. Distilled water spike and recovery experiments indicate that at concentrations equal to or greater than 1.0 microgram per liter, recoveries for most VCH by PT-GC/MS and POCl exceed 80 percent with relative standard deviations of less than 10 percent. Ground-water samples collected from a site on Cape Cod, Massachusetts, where a shallow, unconfined aquifer has been contaminated by VCH also were analyzed. Results from PT-GC/MS and POCl analyses of duplicate sets of ground-water samples were statistically similar and indicated little bias for either method. Similar conclusions about concentrations and distributions of VCH in the contamination plume were drawn from the two data sets. However, only PT-GC/MS analyses provided information on the individual compounds present in the ground water.

INTRODUCTION

Volatile chlorinated hydrocarbons (VCH), such as chlorinated ethenes and ethanes, are among the most commonly detected organic contaminants in ground water (Zoeteman and others, 1980, Council on Environmental Quality, 1981; Page, 1981; Westrick and others, 1984). Reasons for the frequency of VCH detection include their widespread use, their high water solubilities, their resistance to biodegradation, and their relative ease of measurement. Compounds such as tri- and tetrachloroethene are listed as priority pollutants, and have maximum contaminant levels of 5 µg/L (micrograms per liter) (U.S. Environmental Protection Agency, 1987). The presence of these compounds at small concentrations can render ground water unsuitable for potable use (U.S. Environmental Protection Agency, 1985).

The preferred method of analysis for VCH is purge and trap gas chromatography/mass spectrometry (PT-GC/MS) (U.S. Environmental Protection Agency, 1984). This method has a detection limit of approximately 0.2 to 1.0 µg/L, and is used to identify and quantify individual VCH compounds. Once the identities of individual VCH have been determined, it may not be necessary to rely solely on PT-GC/MS to monitor their fate and transport. Collective measurements, such as total purgeable organic chloride (POCl), may be sufficient for some monitoring purposes. Although laboratory and wastewater-treatment studies have indicated the utility of using surrogate measurements in place of specific compound analysis (Jekel and Roberts, 1980; McCarty and Aieta, 1984; Stevens and others, 1985), their usefulness in evaluating ground-water contamination has not been well documented.

This paper describes a field/laboratory study that was conducted to evaluate the utility of using POCl as a surrogate measurement for PT-GC/MS when monitoring VCH in ground water. Quantitative relations between surrogate and specific compound measurements in distilled water and ground water samples were determined. From analysis of environmental samples, the distribution of VCH in a plume of contaminated ground water was established.

SITE DESCRIPTION

The field study was conducted at the U.S. Geological Survey's Cape Cod Toxic-Substances Hydrology Research site, located approximately 80 kilometers south of Boston, Mass. (fig. 1). This site is the location of a plume of contaminated ground water resulting from disposal of secondary-treated sewage effluent by rapid infiltration into a shallow, unconfined sand and gravel aquifer (LeBlanc, 1984). The plume contains concentrations up to several hundred micrograms per liter of dichloroethene, trichloroethene, and tetrachloroethene (Thurman and others, 1986; Barber and others, 1988). Because of the extensive nature of the contamination plume (more than 3,500 m (meters) long, 1,000 m wide, and 30 m thick), analysis of hundreds of samples are required to monitor the transport and long-term fate of VCH in the aquifer.

SAMPLING AND ANALYSIS

Ground-Water Sampling

During the spring of 1988, ground-water samples were collected from 197 wells at 62 locations and analyzed for VCH. Location of wells discussed in this report are shown in figure 1. The samples were obtained from PVC-cased monitoring wells by either a stainless-steel submersible pump or a peristaltic pump, depending on the well-casing diameter. Both pumps were fitted with Teflon[4] tubing. At each well, a minimum of three casing volumes were evacuated prior to sampling to ensure that standing water was purged. The specific conductance of the pump outflow was monitored, and samples were collected after values had stabilized. At each location, separate samples for PT-GC/MS and POCl analysis were collected without headspace in 40 mL (milliliter) amber vials with Teflon-lined silicon septa, and stored at 4 °C (degrees Celsius). Analysis was performed within 2 weeks of sample collection.

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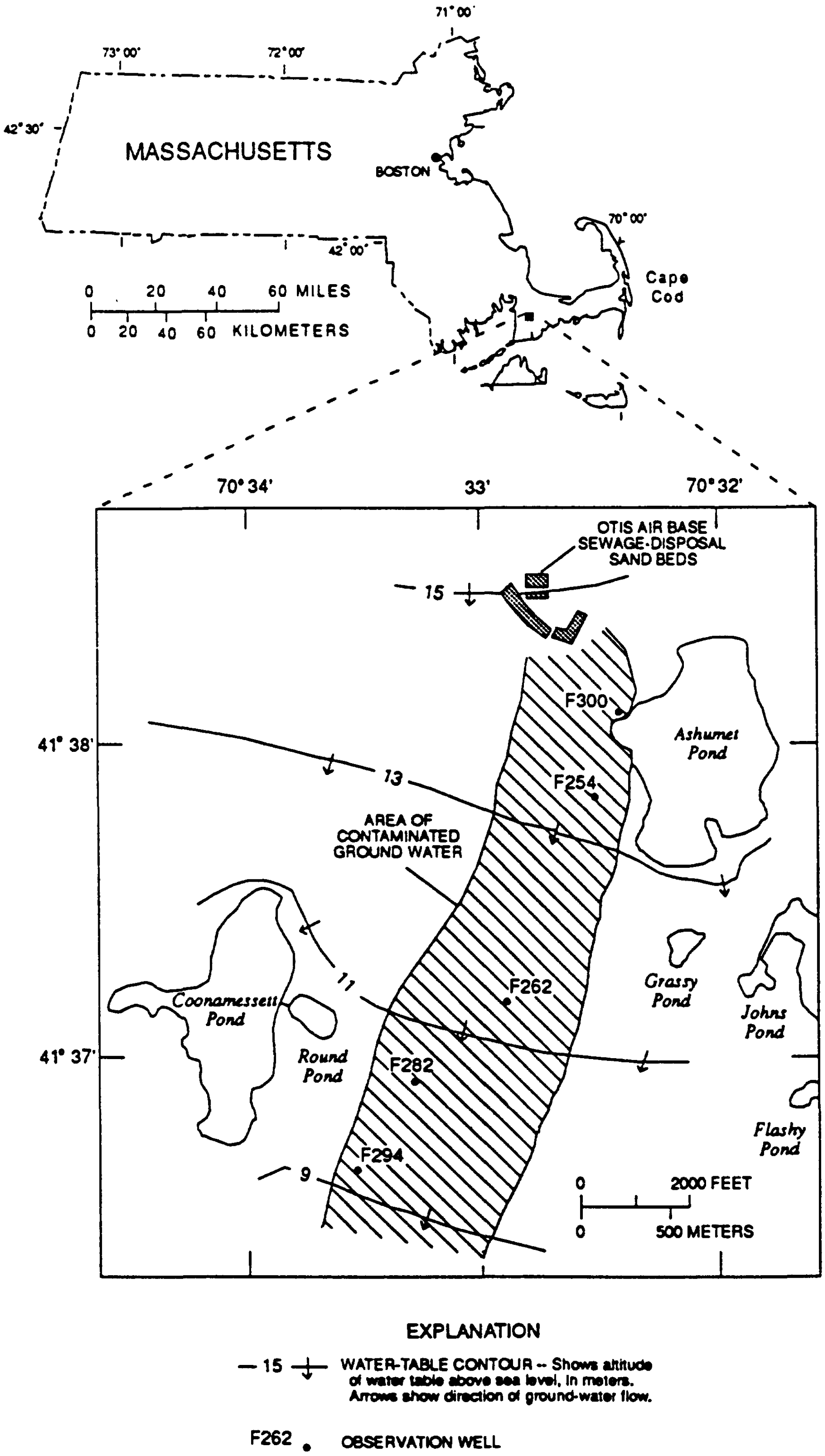
[1] U.S. Geological Survey, Denver, Colo.

[2] U.S. Geological Survey, Lawrence, Kans.

[3] Dohrmann Rosemount Analytical Division, Santa Clara, Calif.

[4] The use of brand, firm, or trade names is for identification purposes only and does not imply endorsement by the U.S. Geological Survey.


71°00'
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OTIS AIR BASE SEWAGE-DISPOSAL SAND BEDS
15
13
11
9
AREA OF CONTAMINATED GROUND WATER
F300
F254
F262
F282
F294
Ashumet Pond
Coonamessett Pond
Round Pond
Grassy Pond
Johns Pond
Flashy Pond
0 2000 FEET
0 500 METERS
EXPLANATION
15 WATER-TABLE CONTOUR -- Shows altitude of water table above sea level, in meters. Arrows show direction of ground-water flow.
F262 ● OBSERVATION WELL

Figure 1. Site location map showing wells sampled in this study. Data for wells with numbers are given in table 1.

Analytical Methods

The PT-GC/MS analysis was a modification of USEPA Method-624 (U.S. Environmental Protection Agency, 1984). A 25-mL water sample was purged with helium, purged compounds were trapped on Tenax/Carbosieve/Silica gel adsorbent, and the adsorbent was thermally desorbed onto a 2.5-m long x 2-millimeter inside-diameter glass-gas chromatography (GC) column packed with 60/80 mesh Carbopack. The GC oven had an initial temperature of 45 °C for 4 minutes, followed by an 8 °C per minute ramp to 220 °C where the temperature was held for 21 minutes. Electron-impact mass spectra were acquired scanning from 45 to 310 atomic mass units (0.5 scan per second). Compound identification was based on matching of mass spectra and chromatographic retention times with standards. Quantitation was based on internal standards and a six-point calibration curve.

POCl was measured by sparging the sample with oxygen, combusting the sparge gas at 900 °C to form carbon dioxide and hydrogen chloride gas, accumulating the hydrogen chloride reaction product in a coulometric titration cell containing 70 percent acetic acid/water solution, and titrating the free chloride with silver ion to form a silver chloride precipitate. The quantity of titrant consumed was measured by microcoulometry. Daily calibration was done by injecting 1 microliter of a 1,1,1- trichloroethane/methanol solution containing 50 and 500 nanograms of organic chloride per microliter directly into the sparge vessel. Aqueous standards also were analyzed daily.

RESULTS AND DISCUSSION

Laboratory Studies

Distilled water spike and recovery studies (10 replicates) for several VCH indicate that at concentrations of 1.0, 10, and 100 μg/L, recoveries by PT-GC/MS are greater than 85 percent, and average relative standard deviations (RSD) are about 10 percent. At a concentration of 0.2 μg/L, all of the compounds were detected, although recovery and precision were poorer than achieved at the larger concentrations.

Similar spike and recovery experiments for POCl analysis (four replicates) indicate that at concentrations of 1.0, 10, and 50 μg/L, recoveries were generally 80 percent or greater with an average RSD of around 10 percent. Although all of the compounds were detected at a concentration of 0.2 μg/L, their recovery and precision decreased dramatically relative to the higher concentrations.

Results of analyses of distilled-water blanks indicate that laboratory contamination is not significant. Likewise, carryover between samples was not detected.

Field Study

PT-GC/MS analysis of the 197 field samples provided results that were similar to those measured previously at the site (Thurman and others, 1986; Barber and others, 1988). Only three VCH were detected either frequently or at large concentrations; 1,2-dichloroethene (combined cis and trans isomers), trichloroethene, and tetrachloroethene. Other compounds detected less frequently or at low concentrations include 1,1-dichloroethene, 1,1- and 1,2-dichloroethane, 1,1,1-trichloroethane, trichloromethane, and tetrachloromethane. Table 1 summarizes the results of PT-GC/MS analysis for select ground-water samples collected along a longitudinal transect of the plume. These data show the variability in relative proportions and concentrations of individual compounds as a function of distance from the infiltration beds and depth below land surface.

To compare the results from PT-GC/MS analysis with POCl data, concentrations of individual VCH determined by PT-GC/MS were converted to equivalent mass of organic chloride, and the individual values were summed to give the total amount of organic chloride determined by PT-GC/MS analysis (PT-POCl). A comparison of measured POCl and calculated PT-POCl values for select wells is presented in table 1. Differences in concentrations between the two methods were generally less than 5 percent, although some samples had differences of more than 10 percent. When no VCH were present at concentrations greater than the detection limit of PT-GC/MS, total POCl values were usually less than 1.0 μg/L.

The PT-POCl concentrations for all of the analyses are plotted as a function of POCl concentrations in figure 2. Least-squares linear regression analysis was used to identify the relation between concentrations for the two methods. There is a highly significant positive correlation between the data obtained by the two analytical methods (r^2= 0.98), the slope of the equation (POCl coefficient) is slightly greater than unity, and the intercept is near zero. Results of paired t-test analysis indicate that the results from the two analytical methods are not significantly different at α = 0.05. Samples with VCH concentrations below the detection limit for PT-GC/MS and POCl were assigned concentrations of 0.2 μg/L (detection limit), 0.1 μg/L (one-half the detection limit), and zero. The effect of the various censoring methods, as well as complete elimination of samples with concentrations less than the detection limit from the statistical analysis, did not significantly affect the results.

On average, concentrations determined by PT-POCl are slightly less than those determined by POCl. This slight positive bias for POCl may result from the presence of individual compounds at concentrations less than the PT-GC/MS detection limit that are detectable by POCl analysis when measured as the sum of all compounds. Twenty-nine percent of the samples had VCH concentrations less than 0.2 μg/L by PT-POCl and 20 percent had VCH concentrations less than 0.2 μg/L by POCl. Twenty-six percent of the samples had concentrations between 0.2 to 1.0 μg/L by PT-POCl and 34 percent had concentrations between 0.2 to 1.0 μg/L by POCl. The frequency of detection was equal for PT-POCl and POCl in the concentration ranges of 1.0 to 10.0 μg/L, 10 to 50 μg/L, 50 to 100 μg/L, and greater than 100 μg/L.

Interpretation of field data with respect to fate and transport of VCH on the basis of the PT-GC/MS and POCl data resulted in the same general conclusions because the two data sets were nearly identical in terms of spatial distribution and absolute concentrations. However, only the

Table 1. *Purge and trap gas chromatography/mass spectrometry, purge and trap purgeable organic chloride (PT-POCl), and purgeable organic chloride (POCl) data for select ground-water samples*

[DCEe=dichloroethene; DCEa=dichloroethane; TCEe=trichloroethene; TCEa=trichloroethane; TTCEe=tetrachloroethene; TCM=trichloromethane; concentration in µg/L for individual compounds and µg Cl/L for POCl and PT-GC/MS]

Sample[1]	Distance[2]	1,1-DCEe	1,2-trans DCEe	TCEe	TTCEe	1,1-DCEa	1,1,1-TCEa	TCM	PT-POCl	POCl
F300-10	500	<0.2	<0.2	<0.2	1.0	<0.2	<0.2	<0.2	1.0	<0.2
F300-30		<.2	.3	1.5	.4	< .2	<.2	<.2	1.8	1.5
F300-50		<.2	<.2	<.2	<.2	<.2	<.2	<.2	.0	.2
F300-73		<.2	<.2	.2	.6	<.2	<.2	<.2	.7	.3
F300-99		<.2	<.2	1.8	4.9	<.2	<.2	.6	6.2	2.8
F254-26	900	<.2	.3	<.2	<.2	<.2	<.2	.3	.5	.8
F254-54		<.2	5.1	3.7	1.0	<.2	<.2	<.2	7.5	6.2
F254-72		<.2	240	22	530	5.0	<.2	<.2	237	206
F254-107		<.2	8.7	9.0	14	<.2	1.2	<.2	27	19
F254-140		<.2	2.4	20	.3	<.2	.6	<.2	19	16
F254-168		<.2	<.2	<.2	<.2	<.2	<.2	<.2	.0	2.0
F254-216		<.2	<.2	<.2	<.2	<.2	<.2	<.2	.0	1.2
F262-41	2,200	<.2	<.2	<.2	.3	<.2	<.2	.5	.7	1.4
F262-69		<.2	.5	14	91	.8	<.2	<.2	90	80
F262-85		<.2	<.2	5.1	21	<.2	<.2	<.2	22	20
F262-109		.4	3.9	27	5.8	.9	1.4	<.2	32	28
F262-159		<.2	<.2	.6	<.2	<.2	<.2	<.2	.5	.8
F282-49	2,900	< .2	<.2	<.2	2.1	< .2	< .2	1.8	3.4	1.5
F282-70		<.2	1.6	53	80	<.2	<.2	.5	198	140
F282-94		.2	<.2	8.0	15	<.2	1.3	<.2	21	21
F282-123		<.2	<.2	<.2	<.2	<.2	<.2	<.2	.2	.5
F294-64	3,500	<.2	<.2	<.2	<.2	<.2	<.2	1.1	1.0	2.2
F294-77		<.2	<.2	8.2	10	<.2	.5	.5	16	15
F294-89		<.2	<.2	15	8.3	<.2	.7	<.2	20	9.3
F294-109		<.2	<.2	<.2	<.2	<.2	<.2	<.2	.0	.4

[1] Value after hyphen is depth below land surface (in feet).

[2] Distance downgradient from the infiltration bed source (in meters).

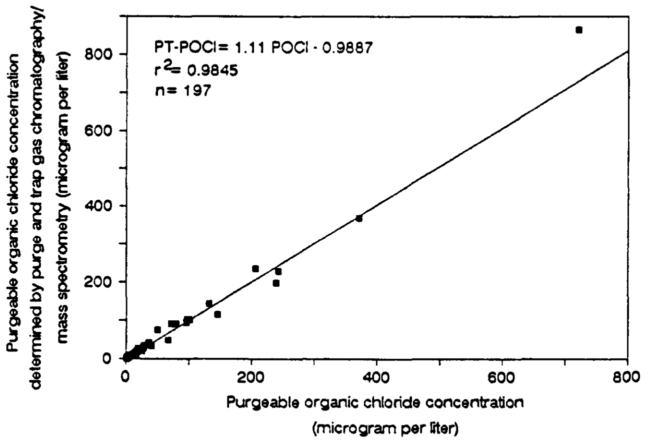

Figure 2. Plot of total purgeable organic chloride concentrations determined by purge and trap gas chromatography/mass spectrometry as a function of purgeable organic chloride concentrations. Also shown are linear regression equation, correlation coefficient (r^2), and number of samples used in analysis (n). Solid line is theoretical 1:1 correlation.

PT-GC/MS results provided data on the relative concentrations of the individual VCH compounds present. These data are needed for complete interpretation of the contamination problem.

Because of the similarity in the results of PT-POCL and POCl analyses, the POCl data provide a secondary measurement for testing the accuracy of PT-GC/MS results; such testing is less expensive than replicate PT-GC/MS analysis on all samples. POCl analysis also was useful for screening samples prior to PT-GC/MS analysis. Concentrations of VCH in samples analyzed in this study ranged from less than the detection limit to more than 100 µg/L over a 20-foot vertical profile. By analyzing for POCl first, samples that have no detectable concentrations of VCH can be eliminated (with appropriate check samples), or analyzed under more sensitive conditions. In this study, 29 percent of the samples had VCH concentrations less than the PT-GC/MS detection limit; all of these samples were identified as having very low VCH concentrations by POCl analysis. POCl analysis also identified samples with very high concentrations, which can cause quantitation errors and contaminate the GC/MS system. About 20 percent of the samples in this study had concentrations that required dilution for GC/MS analysis, all of which were identified by POCl analysis. The use of POCl analysis as a supplementary analysis for VCH can provide efficient use of analytical resources.

SUMMARY

The results of this study indicate that noncompound-specific POCl analysis can be used to monitor ground water contaminated by VCH. The utility of this method is enhanced when the compound-specific nature of the contamination problem has been determined previously by PT-GC/MS analysis, or when the objective of the investigation is to monitor the total mass of VCH. Likewise, POCl analysis can be used as a laboratory tool to screen samples for nondetectable and very large concentrations of VCH prior to PT-GC/MS analysis.

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EFFECTS OF PARTICLE SIZE AND MINERALOGY ON SORPTION OF NONIONIC ORGANIC SOLUTES TO GLACIAL OUTWASH SEDIMENTS, CAPE COD, MASSACHUSETTS

By Larry B. Barber, II[1]

ABSTRACT

Transport of organic contaminants in ground water is controlled by sorption to aquifer sediments. However, the effects of sediment geochemical properties on sorption and transport are poorly understood. In this study, the sorption of nonionic organic compounds onto sediment particle size and mineralogical fractions from a glacial outwash aquifer on Cape Cod, Massachusetts, was evaluated. Sediment organic carbon (SOC) and surface area of the aquifer sediments increased with decreasing particle size. Abundance of magnetic minerals also increased with decreasing particle size. SOC and surface area were 5 to 10 times greater for the magnetic mineral fraction than for the nonmagnetic mineral fraction. Batch equilibrium-isotherm experiments were conducted using tetrachlorobenzene (TCB), pentachlorobenzene (PCB), and 2,6-di-t-butyl-benzoquinone (DTBB). For a given solute, sorption increased with decreasing particle size (increasing SOC). For a given particle size fraction, the magnetic minerals had higher SOC and greater sorption than did the bulk sediment or nonmagnetic minerals. Although SOC content was typically <0.1 percent, sorption was consistent with a partition mechanism, and measured uptake of TCB and PCB was close to that predicted based on their octanol/water partition coefficients. At SOC contents <0.01 percent, sorption was slightly greater than predicted, possibly because of mineral surface interactions. Removal of SOC from the magnetic minerals by hydrogen-peroxide treatment decreased sorption of PCB in proportion to the decrease in SOC (about 50 percent). However, significant uptake of PCB after SOC removal, and the nonlinearity of the isotherm for the treated minerals indicate that adsorption is contributing to uptake.

INTRODUCTION

The mechanism of sorption for nonionic organic compounds (NOC) onto soils with relatively high (>0.1 percent) sediment organic carbon (SOC) content has been extensively studied, and is generally considered to be a partition process (Chiou and others, 1983; Chiou, 1989). On the other hand, sorption of NOC onto low-SOC aquifer sediments, and the relation to physical (particle size) and geochemical properties (mineralogy, grain coatings) of aquifer sediment is a relatively new area of study.

The objective of this study was to evaluate the effect of physical and geochemical properties of aquifer sediments on the sorption and ground-water transport of NOC. A conceptual model was developed using particle size as a couple between hydrological (flow velocity) and geochemical (sorption) aspects of transport (Barber, 1987, 1989, 1990; Barber and others, in press). Particle size is the dominant sediment factor affecting the magnitude of hydraulic conductivity (K_h). With decreasing particle size, there is a concomitant decrease in K_h that controls the flow-velocity term in the advection-dispersion solute-transport equation (Freeze and Cherry, 1979). Several studies (Karickhoff and others, 1979; Schwarzenbach and Westall, 1981; Hand and Williams, 1987) report an inverse relation between sorption of NOC and particle size, whereby the amount of sorption increases as particle size decreases. SOC also increases with decreasing particle size, and the increased sorption is attributed to partitioning of NOC into SOC. The increase in SOC with decreasing particle size is generally considered to be a function of the large surface area of fine-grained material. However, it has long been known that sediments become enriched in heavy minerals as particle size decreases because of geological, mineralogical, and sedimentological factors (Rubey, 1933; Rittenhouse, 1943). Thus, it is proposed here that the relation between increasing SOC content with decreasing particle size is a function of mineralogical composition rather than surface area.

The surface chemistry of iron-rich heavy minerals differs from that of quartz and feldspar. Heavy minerals and their weathering products tend to have positive surface charge at pH conditions of most ground waters (pH 4 - 8), whereas quartz and feldspar have negative surface charge. Positively charged surfaces of iron oxides and hydroxides provide sites for electrostatic, ligand exchange, and specific adsorption reactions with dissolved organic matter which is rich in carboxylic and phenolic functional groups that impart a net negative charge to the molecule (Tipping, 1981; Davis, 1982; Jardine and others, 1989; Murphy and others, 1990). The result of interaction between dissolved organic matter and positively charged surfaces is preferential enrichment of SOC on iron-bearing minerals over that of quartz and feldspar. Because of their higher SOC contents, iron-rich minerals would be expected to have greater sorption capacity for NOC than would quartz or feldspar.

This paper describes a study conducted to determine the relation between sediment-particle size, mineralogy and sediment organic carbon in the glacial outwash of the Cape Cod aquifer. Laboratory sorption experiments were conducted to determine the sorption behavior of NOC for the various sediment fractions.

METHODS

The effect of particle size and mineralogy on the sorption of NOC was evaluated using aquifer sediments collected from several locations at the Cape Cod Toxic-Substances Hydrology Research site near Falmouth, Mass. (fig. 1). This site has an extensive plume of contaminated ground water as the result of disposal of secondary-treated

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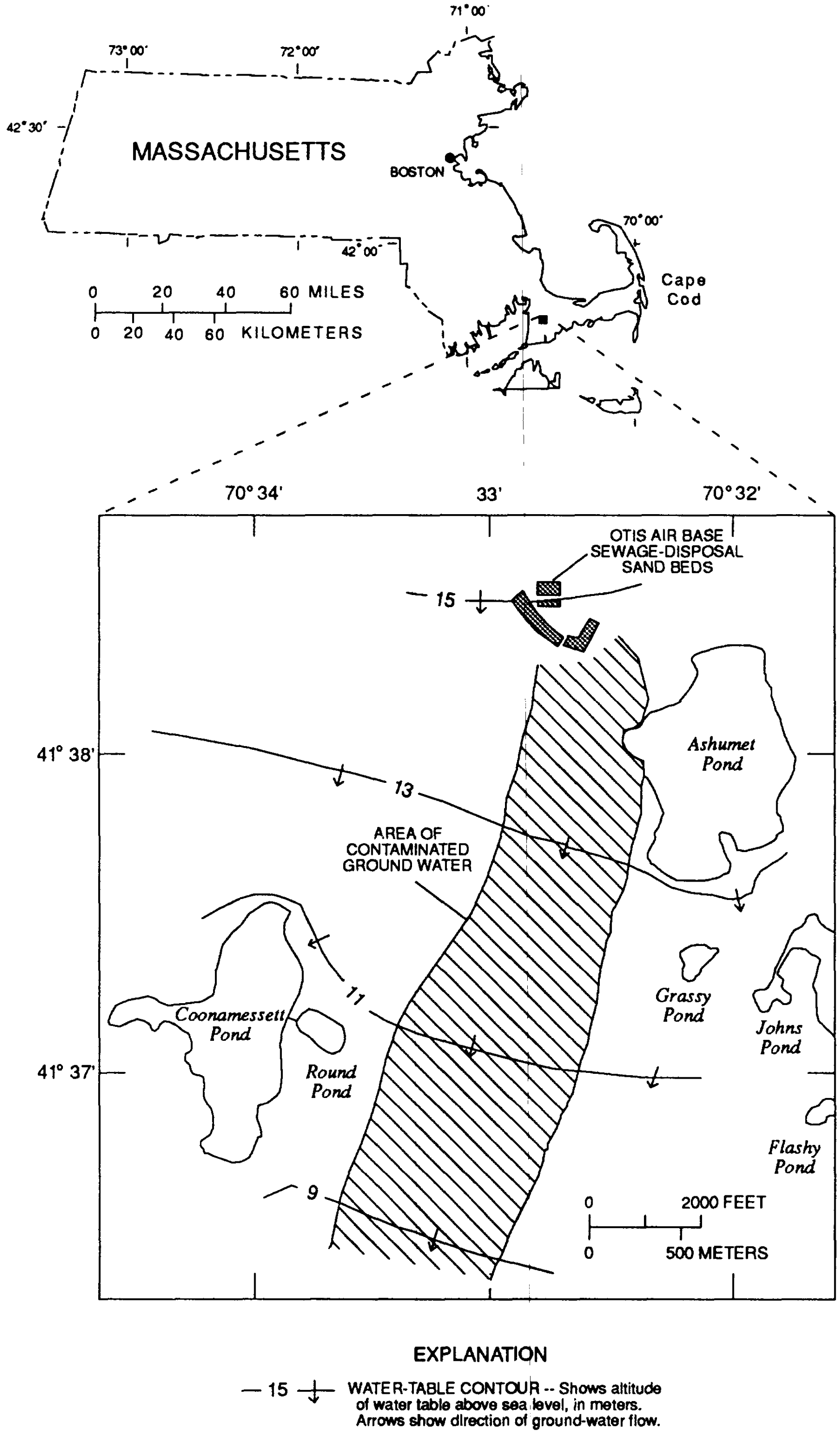
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Round Pond
Flashy Pond
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0 2000 FEET
0 500 METERS
EXPLANATION
— 15 WATER-TABLE CONTOUR -- Shows altitude of water table above sea level, in meters. Arrows show direction of ground-water flow.

Figure 1. Study area location map.

sewage effluent into sand infiltration beds (LeBlanc, 1984; Barber and others, 1988). The aquifer at the site consists of unconsolidated sand and gravel glacial outwash of Pleistocene age. Details on the geology of the site can be found in Mather and others (1942), Ziegler and others (1964) and Oldale (1976).

The sediments were collected with a wireline-piston coring method described by Zapico and others (1987). The sediments were characterized and fractionated by methods described by Barber (1987; 1990). An eight-fold particle-size separation [<63 μm (micrometers); >63 to <125 μm; >125 to <250 μm; >250 to <500 μm; >500 to <1,000 μm; >1,000 to <2,000 μm; >2,000 to <4,000 μm; and >4,000 μm) was done by standard sieve methods. The >63 to <125 μm, >125 to <250 μm, and >250 to <500 μm fractions were separated based on magnetic susceptibility. SOC of the various magnetic and particle-size fractions was determined by high-temperature oxidative combustion with coulometric detection. Surface area was determined by nitrogen gas adsorption. Mineralogy of the sediment fractions was determined by optical microscopy and x-ray diffraction.

Equilibrium-batch sorption isotherm experiments were conducted using tetrachlorobenzene (TCB), pentachlorobenzene (PCB) and 2,6-di-t-butyl-benzoquinone (DTBB) as solutes and various particle size and magnetic fractions as sorbents. Pure water solubilities for TCB, PCB, and DTBB are 0.60, 0.56, and 2.7 milligrams per liter respectively. The isotherm experiments involved adding 4 grams of sediment to 20 milliliters of distilled water, spiking the slurry at a range of concentration from 0.1 to 50 percent of the pure water solubility of the solutes of interest, equilibrating the sediment/water mixture for 48 hours on a shaker table, and separating the phases by centrifugation at 6000 revolutions per minute for 1 hour. The aqueous phase was then extracted with hexane, and analyzed by capillary gas chromatography/mass spectrometry. The amount of sorption was determined by difference in solution phase concentrations of the solutes after equilibration with the sediment with respect to control samples in which no sediments were added. All data points were determined in duplicate or triplicate.

RESULTS AND DISCUSSION

There is a functional relation between abundance of magnetic minerals and particle size. The nonmagnetic fraction consists predominantly of quartz and feldspar, whereas the magnetic fraction consists of a suite of minerals and mineral groups, including glauconite, goethite (limonite), hematite, magnetite, biotite, amphibole, pyroxene, chlorite, tourmaline, garnet, and epidote. However, glauconite, goethite (limonite), and opaque iron oxides predominate. Most of the accessory minerals are isolated in the magnetic fraction, and the abundance of minerals other than quartz and feldspar, determined by point counts of thin sections and by mass of magnetic minerals, is similar. The proportion of the magnetic-mineral fraction increases from <5 percent in the >250 to <500-μm size material to 25 percent in the <63 μm-fraction.

In general, SOC is low, and concentrations for the bulk sediment rarely exceed 0.01 percent. There is an approximately tenfold increase in SOC between the >250 to <500-μm and <63-μm size fractions (table 1). The spatial distribution of SOC for the bulk sediment is variable, and highest concentrations are found in the shallowest sediments, most likely the result of leaching of organic matter from the soil horizon. Also, when the contaminant plume is encountered, SOC increases slightly. Within a given particle-size fraction, SOC content of the magnetic minerals is about 10 times greater than that of the nonmagnetic minerals (table 1). Although magnetic minerals comprise only 5 to 25 percent of the total sediment, they contain 50 to 80 percent of the SOC. The large SOC content of the magnetic minerals is consistent with a surface-charge model for preferential association of dissolved organic matter with iron-bearing minerals.

Surface area follows a trend similar to that of SOC, and increases from 0.5 m^2/g (meters squared per gram) for the >250 to <500-μm particle-size fraction to 8 m^2/g for the <63-μm particle-size fraction (table 1). For the >125 to <250-μm particle-size fraction, the magnetic minerals have a 50 times greater surface area (14 m^2/g) than the nonmagnetic minerals (0.3 m^2/g). The greater surface area of the magnetic minerals is likely the result of the large internal porosity of glauconite and limonite, which are composed of microcrystalline aggregates.

Results of isotherm experiments for TCB and PCB indicate that, even at very low SOC contents, sorption can be measured on most of the sediment fractions (table 1). However, at carbon contents of <0.01 percent, determination of uptake becomes less reliable. Sorption of TCB and PCB increases with decreasing particle size--a trend similar to that of SOC. PCB uptake is greater than TCB uptake, consistent with the greater hydrophobicity (lower pure-water solubility, higher octanol/water partition coefficient, K_{ow}) of PCB. DTBB, which is the most water soluble of the compounds studied, sorbs the least. However, DTBB data are complicated by the presence of the compound on the sediments because of its sorption from the contaminated ground water at the site. For a given particle size, sorption of the magnetic fraction was much greater than sorption of the bulk or nonmagnetic fractions.

In general, experimental sorption data are consistent with partitioning of NOC into SOC as the dominant sorption mechanism. Partitioning is indicated by (1) linearity of isotherms over a range of solute concentrations of 0.1 to 50 percent relative to pure-water solubility, (2) increasing sorption with increasing SOC, and (3) increasing sorption with decreasing water solubility (increasing K_{ow}) of the solute. Carbon-normalized distribution coefficients (K_{oc}) are close to those predicted from two independent regression models (table 1) that relate K_{oc} to the solutes K_{ow} and the SOC content (Schwarzenbach and Westall, 1981; Chiou and others, 1983).

Isotherm experiments were conducted for PCB on the untreated magnetic material and magnetic material that had been oxidized with hydrogen peroxide to evaluate whether sorption to the magnetic fraction was solely a function of its higher SOC content. Hydrogen-peroxide digestion removes approximately 50 percent of the SOC. Isotherms for PCB sorption to the untreated magnetic fraction are linear over a concentration range of 0.1 to 50 percent relative to pure-water solubility. Removal of SOC diminishes sorptive

Table 1. *Summary of data for sediment organic carbon (SOC), surface area (SA), sediment/water distribution coefficients (K_d) in mL/ng (milliliter per nanogram), and log organic carbon/water distribution coefficients (K_{oc}) for tetrachlorobenzene (TCB) and pentachlorobenzene (PCB) sorption isotherm experiments*

			TCB		PCB	
Sediment fraction	SOC (percent)	SA (m^2/g)	K_d (mL/ng)	Log K_{oc}	K_d (mL/ng)	Log K_{oc}
<63 µm, bulk	0.054	5.0	7.7	4.2	19	4.6
63 to 125 µm, bulk	.022	2.6	6.7	4.5	14	4.8
125 to 250 µm, bulk	.012	1.1	3.1	4.8	4.0	5.0
125 to 250 µm, nonmagnetic	.010	.3	4.3	4.6	5.8	4.8
125 to 250 µm, magnetic	.062	14	12	4.3	26	4.6
Model 1, predicted[1]	.062			3.8		4.3
Model 2, predicted[2]	.062			3.7		4.2

[1] Schwarzenbach and Westall, 1981.

[2] Chiou and others, 1983.

capacity by about 50 percent (consistent with amount of carbon removal), and results in a nonlinear isotherm. The isotherm for hydrogen-peroxide-treated material is of the Langmuir or Freundlich type. Sorption onto the magnetic material suggests a dual mechanism consisting of partitioning into the organic-matter phase as well as site-specific adsorption. The proposed mechanism of site-specific adsorption is an electron donor-acceptor complex between π-electrons of the aromatic ring and positively charged surface sites on the magnetic minerals.

SUMMARY

Sorption of NOC onto particle size and mineralogical fractions from a glacial outwash aquifer was evaluated. SOC increases by a factor of 10 as particle size decreases from >250 to <500 µm to <63 µm. Magnetic-mineral abundance is a function of particle size, and increases from <5 percent in the >250 to <500-µm fraction to 25 percent in the <63-µm fraction. SOC is preferentially associated with magnetic minerals, and the magnetic fraction contains most of the SOC in the bulk sediment. SOC content and sorption of NOC increases with decreasing particle size. Within a particle-size fraction, the magnetic minerals have higher SOC and greater sorption of NOC than the bulk sediment or nonmagnetic minerals. Although SOC content is typically <0.1 percent, sorption is consistent with a partition mechanism. Removal of SOC from the magnetic minerals by hydrogen- peroxide treatment decreases sorption of PCB by an amount that is proportional to the decrease in SOC (about 50 percent). However, the nonlinearity of the isotherm for the treated minerals indicates that adsorption may contribute to uptake.

Greater sorption of NOC to magnetic minerals compared to that of nonmagnetic minerals is related to preferential association of dissolved organic matter with positively charged mineral surfaces. However, the large surface area of the magnetic fraction may also have an effect. Several important conclusions can be drawn from this study: (1) Mineralogical substrates of aquifer sediments are not uniform in their affinity for interaction with natural and contaminant organic compounds; (2) there is an inverse relation between iron-bearing magnetic minerals and particle size that accounts, at least in part, for the observed increase in SOC sorption with decreasing particle size; (3) SOC is not uniformly distributed throughout aquifers but varies as a function of space, particle size, and mineralogy.

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PERSISTENCE OF LINEAR ALKYLBENZENESULFONATES AND THEIR METABOLITES IN SEWAGE-CONTAMINATED GROUND WATER, CAPE COD, MASSACHUSETTS

By Jennifer A. Field[1], Larry B. Barber, II[2], Jerry A. Leenheer[2], C.E. Rostad[2], *and* K.A. Thorn[2]

ABSTRACT

Linear alkylbenzenesulfonates (LAS) are the most widely used surfactants in detergent formulations, and they are generally considered to be biodegradable. Although the fate of LAS during sewage treatment and their subsequent discharge into surface waters has been thoroughly investigated, few studies have focused on LAS transformation and transport in ground water. This study specifically investigated LAS transport and fate in a plume of sewage-contaminated ground water that has resulted from rapid infiltration of secondary-treated sewage to a sand and gravel aquifer.

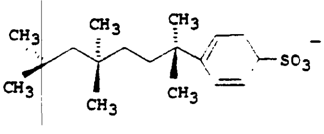
A comprehensive approach involving reverse-phase and ion-exchange chromatography coupled with solvent extraction was used to isolate surfactant-derived contaminants from sewage effluent and ground water. Spectrometric methods, including infrared (IR), ^{1}H-nuclear magnetic resonance (NMR), ^{13}C-NMR, and gas chromatography/mass spectrometry (GC/MS) were used to identify surfactants and their biodegradation intermediates.

LAS and dialkyltetralin (and dialkylindane) sulfonates (DATS) were identified in sewage effluent and in ground water 500 meters downgradient from the point of effluent infiltration. Differences in LAS composition between sewage effluent and ground-water samples indicated preferential removal of external isomers and long-chain homologs during infiltration and ground-water transport. Monocarboxylated DATS biodegradation intermediates were also identified in sewage effluent and ground water. Results indicate that alicyclic contaminants (DATS and DATS-intermediates) are more persistent than their linear analogs. LAS half-life, estimated at 200 days, is an order of magnitude greater than laboratory-derived estimates for LAS biodegradation in ground water.

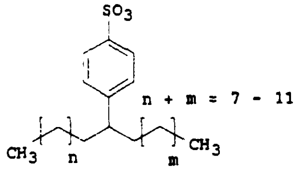
INTRODUCTION

Detergent formulations are complex mixtures of organic and inorganic chemical constituents. Surfactants, builders, foam regulators, solubilizers, fluorescent whiteners, blueing agents, and corrosion inhibitors are examples of compounds typically present in domestic detergent formulations (Jakobi and Lohr, 1987). These components span a wide range of molecular weight, structure, and function. Surfactants are the active cleansing agents in detergent formulations. Surfactants typically comprise 10 to 20 percent, by weight, of detergent formulations.

Alkylbenzenesulfonate surfactants have been major components in detergent formulations since their introduction after World War II. Branched-chain alkyl-benzenesulfonates (ABS) were introduced in the late 1940's as replacements for soaps in laundry and other cleaning formulations (Swisher, 1987). Concern over foaming of waters that receive sewage effluent and ABS accumulation in the environment led detergent manufacturers to switch voluntarily from ABS to linear alkylbenzene sulfonates (LAS) in 1965 (Maehler and others, 1967). The chemical structures of ABS and LAS are shown below:



Isomer of ABS



Generalized structure for LAS

LAS are the dominant surfactants produced and used in many countries (Painter and Zabel, 1989). Domestic detergent formulations account for 77 percent of the 3.64 X 10^8 kilograms of LAS consumed in the United States during 1987 (Chemical Economics Handbook, 1988). This historic change from ABS to LAS, current volume of LAS usage, discharge of LAS to the environment, and potential enhancement of relatively insoluble organic contaminant transport by surfactants (Kile and Chiou, 1989) have focused attention on LAS environmental fate and transport.

Studies of surfactant fate have largely been restricted to surface waters. Certain ground waters differ from other aqueous systems with respect to long residence times, low temperature, low oxygen concentrations, and sparsity of transformation processes (that is, absence of photolysis) that render many ground waters susceptible to long-term contamination. Additional research is required to determine transferability of information about the fate and transport of surfactants in surface waters to ground-water systems.

The field site for this research is the U.S. Geological Survey Cape Cod Toxic-Substances Hydrology Research site (CCTSHRS), located on Cape Cod, Mass. where a plume of sewage-contaminated ground water was created by infiltration of secondary sewage originating from a wastewater-treatment facility. The methylene-blue-active-substances (MBAS) test has been used at CCTSHRS to estimate anionic surfactant concentration and distribution (Barber, 1985; Thurman and others, 1986). ABS surfactants, identified 3,000 m (meters) from the rapid infiltration beds used to receive and dispose of treated wastewater, corresponded to high (2 mg/L (milligrams per liter)) MBAS levels (Thurman and others, 1987). J.A. Field, E.M. Thurman, L.B. Barber, II, and others (U.S. Geological Survey, written commun., 1991) found that LAS accounted for only 4 percent of low MBAS levels (<0.25 mg/L) within 500 m of the infiltration beds. We have hypothesized that LAS sulfophenyl carboxylate metabolites (SPC) contribute to MBAS distributions near (<500 m from) the rapid-infiltration beds.

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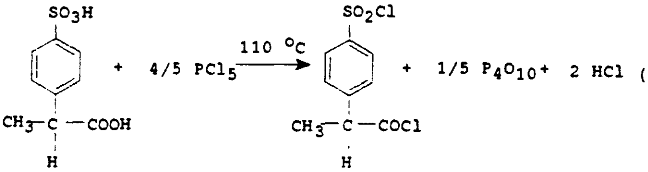
The objective of this research is to determine the fate of LAS in sewage-contaminated ground water. Development of analytical methods to determine LAS, related LAS formulation impurities, and their carboxylated metabolites at detection limits below existing methods was required to meet this objective. This paper relates the results at CCTSHRS for concentrations in ground water of LAS, LAS impurities, and metabolites of LAS to the fate and transport of LAS.

METHODS AND MATERIALS

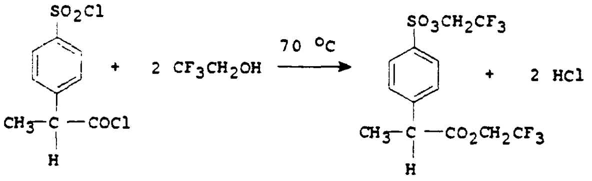
In August 1988, 200 L(liters) of sewage effluent and 200 L of ground water from well F300-50 were collected, filtered, and field-processed for LAS and its degradation intermediates. Well F300-50, located approximately 500 m from the infiltration beds (fig. 1), was sampled at a single point 15 m below land surface for LAS and SPC in ground water. Water-sample collection and processing is described in a report by Field and others (in press). A sequence of methods, depicted in an analytical flowchart (fig. 2), was used to fractionate sewage and ground-water samples. After filtration through a 0.3 micrometer glass-fiber filter, all anions were concentrated on anion-exchange resins and were eluted as the sodium salts. Anion concentrates were shipped to the laboratory where the inorganic anions were removed by desalting the concentrates by reverse-phase chromatography on Amberlite[3] XAD-8 resin. Organic anion concentrates were extracted with methylene chloride at pH 2 to remove neutral and weak-acid surfactants that were related to degradation of nonionic surfactants of the alklyphenol polyethoxylate type. Lastly, reverse-phase chromatography on XAD-8 resin, at pH 12, separated LAS surfactants from SPC degradation intermediates.

Spectrometric characterizations of all fractions (A-E, fig. 2) were performed in the following order of increasing specificity: infrared (IR), proton nuclear magnetic resonance (^{1}H-NMR), carbon-13 nuclear magnetic resonance (^{13}C-NMR), and gas chromatography/mass spectrometry (GC/MS). Infrared spectra of sodium salts of organic anion isolates were obtained in KBr pellets on a Perkin Elmer 580 infrared spectophotometer. Solution-state ^{1}H- and ^{13}C-NMR were run on Varian FT 80A and XL-300 spectrometers. GC/MS with electron-impact (EI) ionization was performed with a Hewlett Packard 5970 Series Mass Selective Detector. GC/MS with negative ion chemical ionization (NCI) was performed using a Finnigan MAT TSQ-46 GC/MS/MS. Detailed sample preparations, standard syntheses, and spectrometer operating conditions are given by Field (1990). Contaminants were identified by comparing field sample spectra to those of standard LAS and SPC.

Trifluoroethyl derivatization with GC/MS analysis (Trehy and others, 1990) was selected for specific identification and quantitation of LAS and SPC. The sulfonate and carboxylic acid groups of LAS and SPC were derivatized to their corresponding trifluoroethylester forms as shown in reactions 1 and 2:



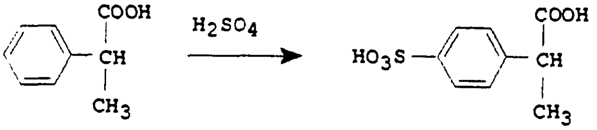
(1)



(2)

Although EI-GC/MS was used extensively for methods development, NCI-GC/MS was used for fraction analysis because of its superior detection limit and selectivity. Molecular ions (M^+) and $(M\text{-}100)^+$ or $(M\text{-}99)^+$, corresponding to loss of 2,2,2-trifluoroethanol, and m/z 163 (trifluoroethylsulfonate) were used to identify and quantify LAS and SPC.

Standard LAS, used in laboratory studies, was reagent grade reference solution lot no. 1288, U.S. Environmental Protection Agency, Cincinnati, Ohio. A suite of C_3, C_6, C_8, and C_{10} sulfophenyl carboxylic acids was synthesized by sulfonation of corresponding phenyl carboxylic acids (Taylor and Nickless, 1979) as shown in reaction 3:



(3)

A C_9 LAS (Proctor and Gamble Co.) and SPC-4 butanoic acid (Monsanto Co.) were used as surrogate internal standards for fraction E and D, respectively.

RESULTS

LAS concentrations, determined by GC/MS, were 90 ± 20 µg/L (micrograms per liter) for sewage effluent and 3 ± 0.7 µg/L for the ground-water sample. Molecular ions for C_{10} to C_{14} LAS were used to determine homolog distribution (fig. 3). Sewage effluent contained C_{10} to C_{14} LAS; however, only C_{10} to C_{12} LAS were detected in the ground-water sample. Comparisons of ^{13}C-NMR spectra of field samples to standards provided evidence for changes in LAS isomer composition. Specific ^{13}C-NMR resonances indicate that external (2-phenyl and 3-phenyl) isomers were diminished in the sewage effluent spectrum and were missing in the ground-water spectrum (Field, 1990).

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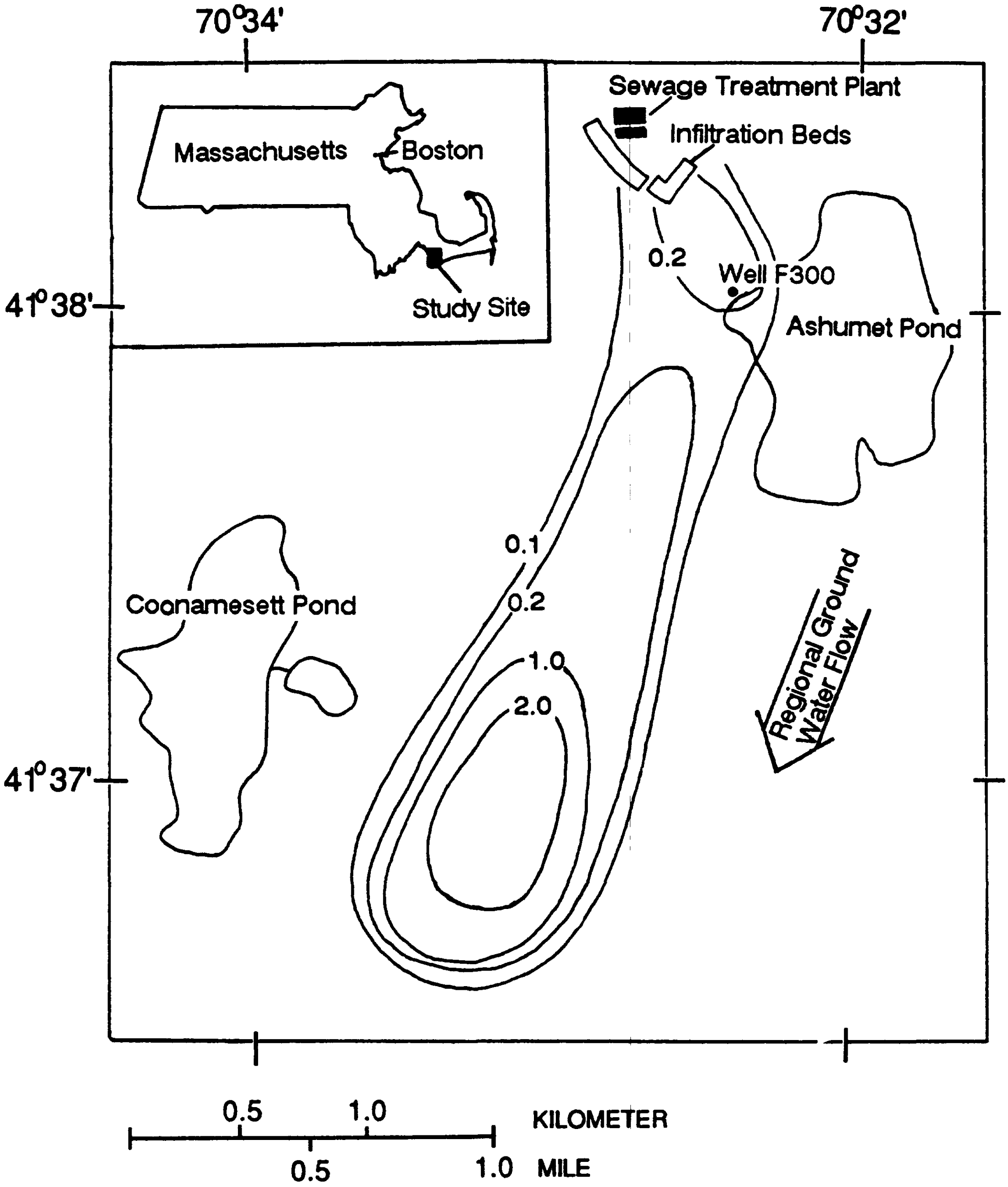
[3] Use of brand, firm, or trade names in this paper is for descriptive purposes only and does not constitute endorsement by the U.S. Geological Survey.


70°34'
70°32'
41°38'
41°37'
Massachusetts
Boston
Study Site
Sewage Treatment Plant
Infiltration Beds
0.2
Well F300
Ashumet Pond
0.1
0.2
1.0
2.0
Coonamesett Pond
Regional Ground Water Flow
0.5
1.0
KILOMETER
0.5
1.0
MILE

EXPLANATION

- 1.0 - Line of equal methylene blue active substances concentration in milligram per liter

Concentration interval is variable

Figure 1. Extent of ground-water contamination as indicated by methylene-blue-active substances in ground water. (Modified from Barber, 1985, fig. 19.)

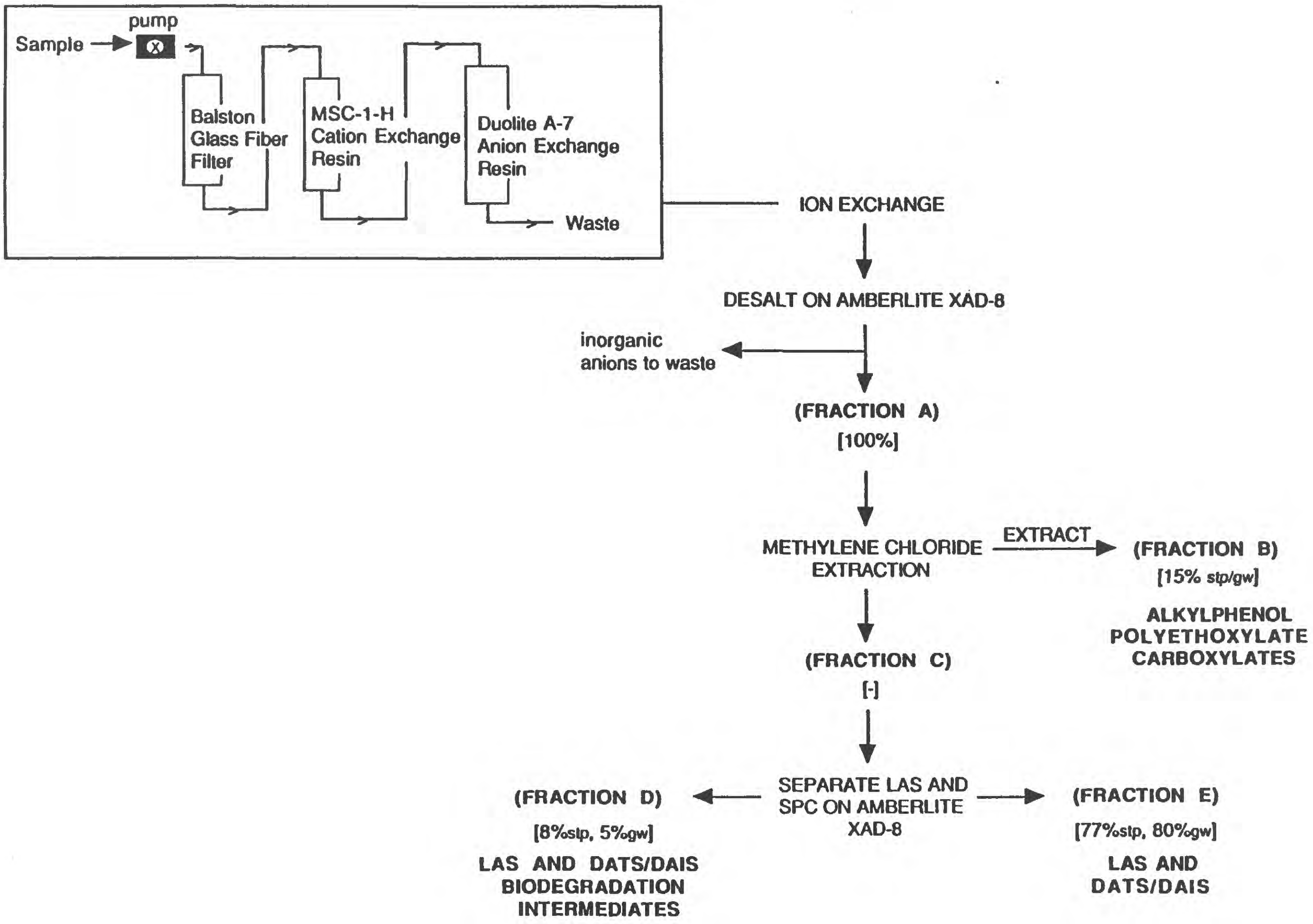

pump
Sample
Balston Glass Fiber Filter
MSC-1-H Cation Exchange Resin
Duolite A-7 Anion Exchange Resin
Waste
ION EXCHANGE
DESALT ON AMBERLITE XAD-8
inorganic anions to waste
(FRACTION A)
[100%]
METHYLENE CHLORIDE EXTRACTION
EXTRACT
(FRACTION B)
[15% stp/gw]
ALKYLPHENOL POLYETHOXYLATE CARBOXYLATES
(FRACTION C)
[-]
SEPARATE LAS AND SPC ON AMBERLITE XAD-8
(FRACTION D)
[8%stp, 5%gw]
LAS AND DATS/DAIS BIODEGRADATION INTERMEDIATES
(FRACTION E)
[77%stp, 80%gw]
LAS AND DATS/DAIS

Figure 2. Preparative scale-fractionation approach used to separate anionic contaminant classes. Fractions listed are given in percent of fraction A to total mass isolated by anion exchange. stp = sewage effluent. gw = well F300-50 ground water.

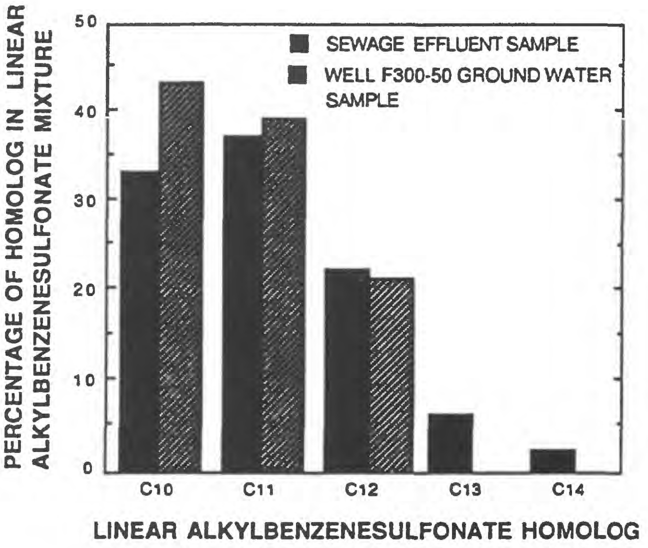


Figure 3. Frequency distributions of linear alkylbenzenesulfonate homologs in sewage effluent and in water sample from well F300-50.

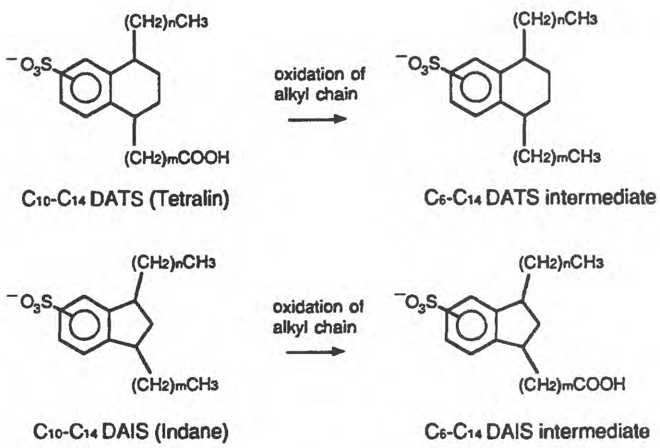

(CH2)nCH3
(CH2)mCOOH
oxidation of alkyl chain
(CH2)mCH3
C10-C14 DATS (Tetralin)
C6-C14 DATS intermediate
C10-C14 DAIS (Indane)
C6-C14 DAIS intermediate

Figure 4. Generalized structure of dialkyltetralin (and dialkylindane) sulfonates and their proposed transformations to carboxylated intermediates.

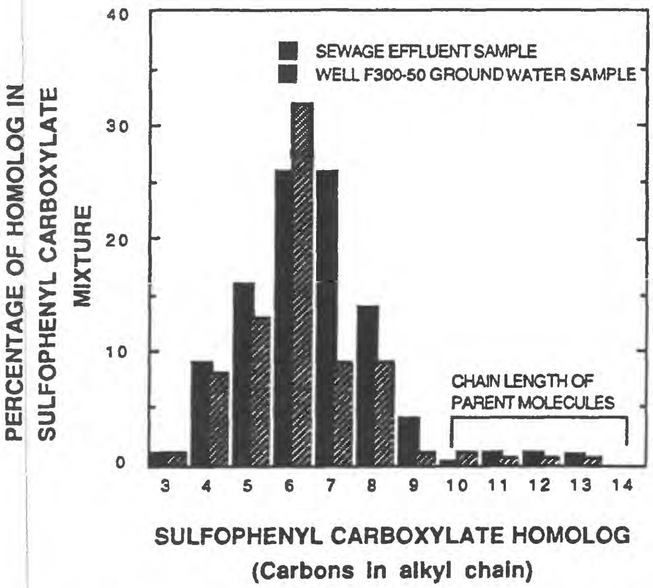


Figure 5. Frequency distribution of sulfophenyl carboxylate metabolite homologs in sewage effluent and in water samples from well F300-50.

A second group of compounds was identified in fraction E. Their NCI fragmentation was similar to that of LAS; however, ions corresponding to (M)$^+$ and (M-100)$^+$ or (M-99)$^+$ were two mass units less than that of their linear analog (LAS). NCI spectra agreed with those of dialklytetralin and dialkylindane sulfonates (DATS) reported by Trehey and others (1990). DATS are alicyclic byproducts formed during the alkylation of benzene with olefins. They are minor components (0.4 to 14 percent by weight) of LAS formulations (Drozd and Gorman, 1988). The chemical structures of tetralin and indane DATS differ from LAS by two mass units (fig. 4). DATS concentrations were estimated, assuming equivalent response factors to C9 LAS, to be 16 ± 4 µg/L in the sewage effluent, and 5 ± 1 µg/L in the ground-water sample.

Monocarboxylated SPC were detected in fraction D of the sewage effluent and ground-water samples. Total SPC concentrations, calculated by means of SPC-4 butanoic NCI quantitation curves, were 51 ± 5 µg/L for the sewage effluent and 8 ± 0.8 µg/L for the ground-water sample. SPC homolog distributions (fig. 5) indicated SPC containing 3 to 12 alkyl chain carbons. Dominant SPC homologs were characterized by intermediate chain lengths of six to seven carbons.

Monocarboxylated DATS intermediates were tentatively identified in fraction D of the sewage effluent and ground-water samples. In an analogous manner as LAS, DATS appear to have degraded to carboxylated metabolites as indicated in figure 4. NCI spectra of DATS metabolites contained (M)$^+$ and (M-100)$^+$ or (M-99)$^+$ ions that were two mass units less than their SPC analogs. DATS metabolite concentrations were estimated to be 86 ± 8 µg/L in sewage effluent and 27 ± 3 µg/L in the ground-water sample.

DISCUSSION

As a result of infiltration and ground-water transport, LAS concentrations at well F300-50 were reduced by 97 percent. J.A. Field, E.M. Thurman, L.B. Barber, II, and others (U.S. Geological Survey, written commun., 1991) determined that LAS disappearance occurred primarily during infiltration so that only trace concentrations are transported by ground water. We interpret ^{13}C-NMR and GC/MS results as possibly indicating preferential removal of LAS external isomers and long-chain homologs by sorption and(or) biodegradation processes during infiltration (fig. 3).

Although IR and NMR spectrometry results indicated the presence of SPC (Field, 1990), fraction complexity prevented definitive identification using these techniques. Derivatization of SPC to their corresponding trifluoroethyl esters provided the necessary selectivity and sensitivity for identifying SPC homologs by use of GC/MS. Sewage effluent and ground-water homolog distributions were similar, indicating persistence of intermediate chain-length SPC during infiltration and ground-water transport. (fig. 5).

DATS concentrations were low compared to LAS concentrations in sewage effluent but were equal to LAS in waters from well F300-50. Results indicate that alicyclic structure contributes to the relative persistence of DATS and their intermediates over their linear analogs (LAS and SPC). Although DATS previously have been detected in sewage influent, sewage effluent, riverwater, and sediment (Trehey and others, 1990), this paper represents the first identification of DATS in ground water.

Surfactant-derived contaminants, identified in this study, represented 75 percent of the MBAS concentration of the sewage effluent, and 23 percent of the MBAS concentration for the ground-water sample (fig. 6). LAS, SPC, DATS, and DATS metabolites identified in water from well F300-50 have been transported for a minimum of 2.7 years, assuming a maximum ground-water velocity of 0.5 meters per day (LeBlanc and others, 1987). In the CCTSHRS system, the minimal residence time of LAS was estimated to be 200 days--an order of magnitude greater than that observed for laboratory-derived estimates (Federle and Pastwa, 1988; Larson and others, 1989). However, results indicate that most of the LAS degradation occurred during the infiltration stage (J.A. Field, E.M. Thurman, L.B. Barber, II, and others, U.S. Geological Survey, written commun., 1991), accompanied by a much slower rate of degradation during the ground-water transport stage. More empirical observations of LAS in various environments are needed to evaluate the applicability of laboratory-derived rates of biodegradation to natural systems.

Persistent, low levels of residual LAS in ground water have been attributed to a more microbially resistant mixture of LAS homologs and isomers and to temperature and oxygen concentrations that do not favor LAS degradation compared to many surface-water and laboratory studies of LAS degradation. All surfactant-derived contaminants identified in the CCTSHRS ground water were substantially below toxic thresholds (Kimerle and Swisher, 1977).

CONCLUSIONS

Identification of linear alkylbenzenesulfonates, linear alkylbenzenesulfonate metabolites, dialkyltetralin (and dialkylindane) sulfonates, dialkyltetraline (and dialkylindane) sulfonate metabolites, and alkylphenol polyethoxylate residues demonstrated the utility of a comprehensive analytical approach. Although modern surfactants are largely removed by sewage treatment, very sensitive methods permit detection of low, residual

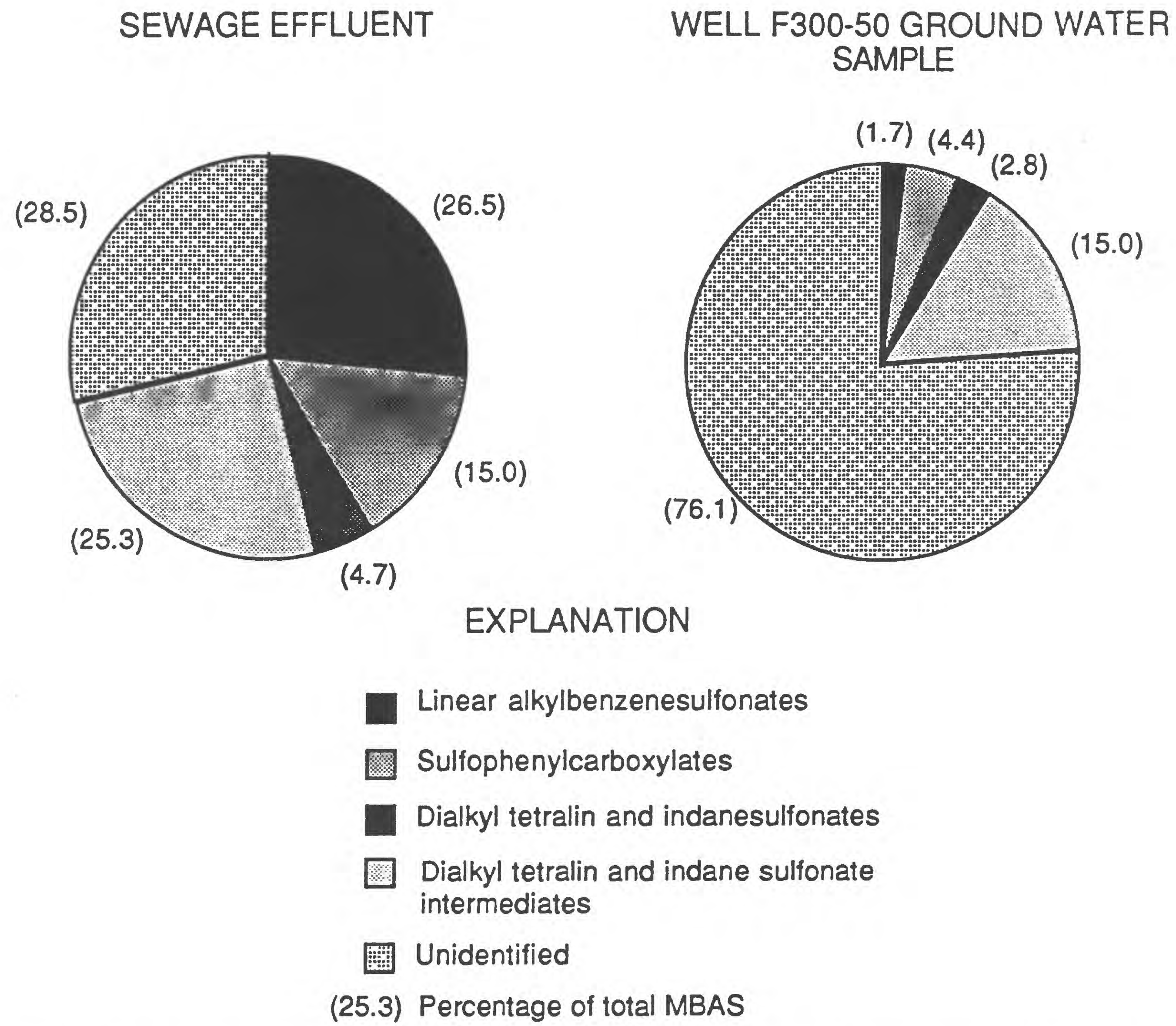


Figure 6. Percentage of methylene-blue-active substances, identified as specific surfactant-derived contaminants, in sewage effluent and water samples from well F300-50.

surfactant-derived contaminants. Identified surfactant-derived contaminants represent chemicals that are resistant to mineralization at trace concentration levels under prevailing geochemical conditions at the Cape Cod Toxic-Substances Hydrology Research site.

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ISOLATION AND CHARACTERIZATION OF AUTOTROPHIC, HYDROGEN-OXIDIZING, DENITRIFYING BACTERIA FROM GROUND WATER AS POTENTIAL AGENTS FOR BIOREMEDIATION OF NITRATE CONTAMINATION

By Richard L. Smith[1] *and* Marnie L. Ceazan[1]

ABSTRACT

Nitrate is a common contaminant of ground water in the United States due to agricultural practices and disposal of human and animal wastes. Nitrate is relatively stable, and therefore persistent, and is mobile in most aquifers. However, nitrate can be utilized by subsurface microorganisms. Denitrification is the microbial process most likely to remove significant quantities of nitrate from ground water because it is a dissimilatory process and it appears to be suitable as a mechanism for in-situ bioremediation because it produces an innocuous end product, nitrogen gas. The selection of an appropriate substrate to add to the subsurface to stimulate denitrification will be critical to its utility as a bioremediation process. Recently, incubations with sediments collected from a nitrate-contaminated aquifer on Cape Cod, Massachusetts, demonstrated that the addition of hydrogen significantly stimulated denitrification. Subsequently, several strains of autotrophic, hydrogen-oxidizing bacteria were isolated from two different sites within the aquifer and then partially characterized. Although little is known about hydrogen oxidation by denitrification, this activity has significant potential for exploitation as a bioremediation process, and further characterization of these microorganisms is currently being conducted within that context.

INTRODUCTION

Bioremediation has recently received considerable interest as a potential tool for *in-situ* treatment of contaminated ground waters (Abelson, 1990). The approach involves identifying a microbial process or processes that will (1) remove or transform a given contaminant, preferably resulting in innocuous products; and (2) either stimulate the indigenous microbial population to induce the process of interest or add nonnative microorganisms that are capable of catalyzing the process. In both cases, the bioremediation approach usually implies that additional constituents (that is, limiting nutrients and(or) exotic organisms) must be introduced into the aquifer over and above the original contaminants already present. Consequently, for bioremediation to be effective and not simply a trade of one set of contaminants for another, the microbial processes to be exploited need to be very carefully chosen and well characterized.

Nitrate is a common contaminant of ground-water systems, originating from a variety of point (primarily septic systems) and nonpoint sources (agricultural fertilization). Although nitrate often appears to be relatively stable and mobile in ground water, it can be assimilated by microorganisms as a nitrogen source during growth and, under anoxic conditions, can serve as a terminal electron acceptor for nitrate-respiring microorganisms. Both processes would remove nitrate from ground water, suggesting that the potential exists for utilizing microbial processes to remediate nitrate contamination in ground water.

As a dissimilatory, energy-generating process that reduces nitrate to nitrogen gas (N_2), denitrification is the microbial process probably most likely to remove significant quantities of nitrate from ground water. Because the process produces an innocuous end product, N_2, denitrification may be well suited as a mechanism for *in-situ* bioremediation of nitrate contamination. Denitrification occurs in anoxic or suboxic conditions, conditions characteristic of many contaminated aquifers, and has been reported to occur in subsurface environments (Smith and Duff, 1988). When nitrate is persistent in ground water, electron-donor availability is commonly the factor that limits denitrification (Smith and Duff, 1988). Consequently, bioremediation by means of denitrification will necessitate the addition of a suitable electron donor to the aquifer to stimulate denitrification. On the basis of preliminary evidence from a nitrate-contaminated aquifer on Cape Cod that indicated that denitrification was stimulated by the presence of hydrogen, we hypothesized that hydrogen would be a reasonable choice to stimulate denitrification during bioremediation. The purpose of this study was to determine whether hydrogen-oxidizing denitrifying bacteria could be isolated from the Cape Cod aquifer and, if so, to begin to characterize the isolates with the expectation that the physiological capability of the isolates will be useful information when designing bioremediation treatments. This paper describes the results of this study.

METHODS AND RESULTS

This study was conducted in an unconfined sand and gravel aquifer located on Cape Cod, Mass., which has an extensive plume of contaminated ground water from the disposal of treated sewage (LeBlanc, 1984). Ground water and core samples were obtained at well sites F347 and F473 (fig. 1) at a depth of 4.1 to 4.7 meters below the water table. Ground-water geochemistry at this depth is characterized by low dissolved oxygen (O_2) concentrations, relatively low and refractory dissolved organic carbon concentrations, and high nitrate concentrations (table 1) (Barber and others, 1988). Previous studies have demonstrated that denitrification was occurring at this depth at site F347 (Smith and others, 1989) and that denitrification within this aquifer was generally electron-donor limited because the addition of a

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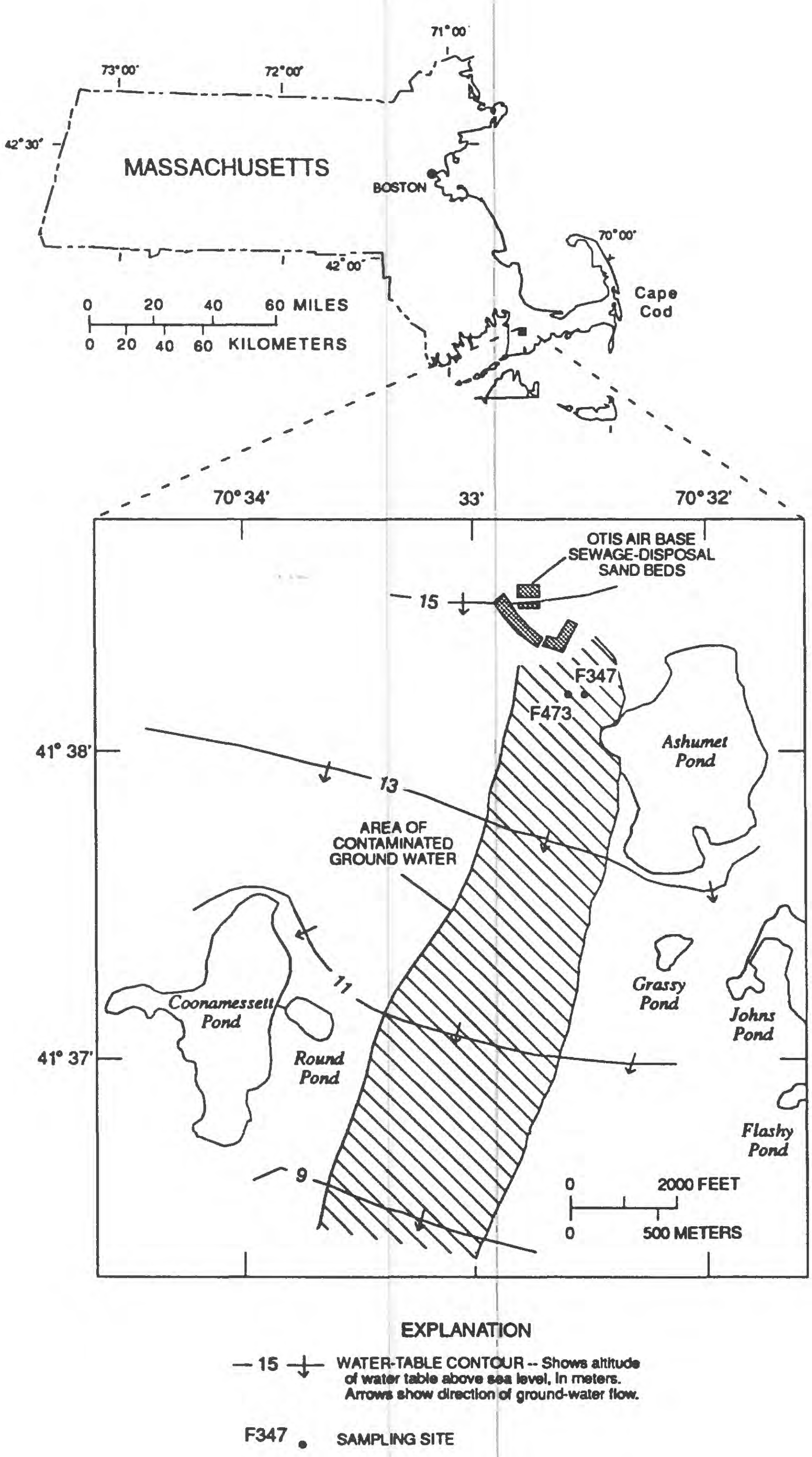
[1] U.S. Geological Survey, Lakewood, Colo.


71° 00'
73° 00'
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MASSACHUSETTS
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70° 34'
33'
70° 32'
OTIS AIR BASE SEWAGE-DISPOSAL SAND BEDS
15
F347
F473
41° 38'
Ashumet Pond
13
AREA OF CONTAMINATED GROUND WATER
Coonamessett Pond
Round Pond
11
Grassy Pond
Johns Pond
41° 37'
Flashy Pond
9
0 2000 FEET
0 500 METERS
EXPLANATION
15 WATER-TABLE CONTOUR -- Shows altitude of water table above sea level, in meters. Arrows show direction of ground-water flow.
F347 ● SAMPLING SITE

Figure 1. Ground water study site on Cape Cod, Massachusetts, showing the location of the contaminant plume and the well sites sampled for this study.

readily oxidizable substrate, such as glucose greatly stimulated the rate of activity in sediment-slurry incubations (Smith and Duff, 1988).

Table 1. *Ground-water geochemistry from the zone of denitrification at well site F347*

[Ground-water sample from 4.7 meters below the water table in June 1990]

Constituent	Concentration
Specific conductance	225 microsiemens per centimeter at 25 degrees Celsius
Oxygen	< 2 micromoles per liter
Nitrate	286 micromoles per liter
Dissolved organic carbon	2.1 milligrams per liter

Glucose is not the only electron donor that can be used to stimulate denitrification within this aquifer. The presence of hydrogen gas (H_2) significantly stimulated the consumption of nitrate in sediment slurries prepared from cores collected at site F347 (fig. 2). Although denitrification is the primary nitrate-consuming mechanism at F347 (Smith and others, 1991, this Proceedings), the endogenous rate of the activity is low relative to *in-situ* nitrate concentrations (fig. 2) and, thus, the activity is generally not assayed using nitrate-consumption curves. However, when H_2 was added, nitrate concentrations of more than 1 millimolar were completely depleted in only 24 hours. This represented more than a hundredfold increase in the rate of nitrate consumption above the endogenous rate and suggested that the denitrifying populations within the aquifer were preadapted to utilize H_2 as an electron donor. This being the case, hydrogen oxidation by denitrification can be considered as a bioremediation treatment for nitrate contamination.

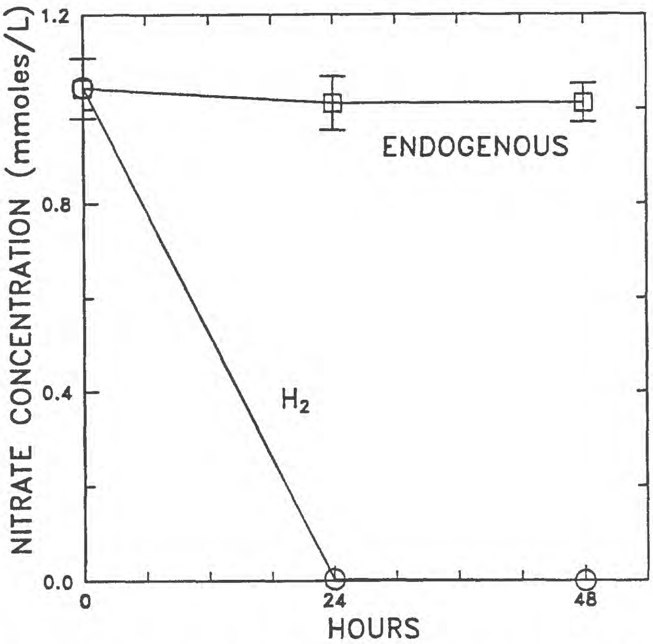
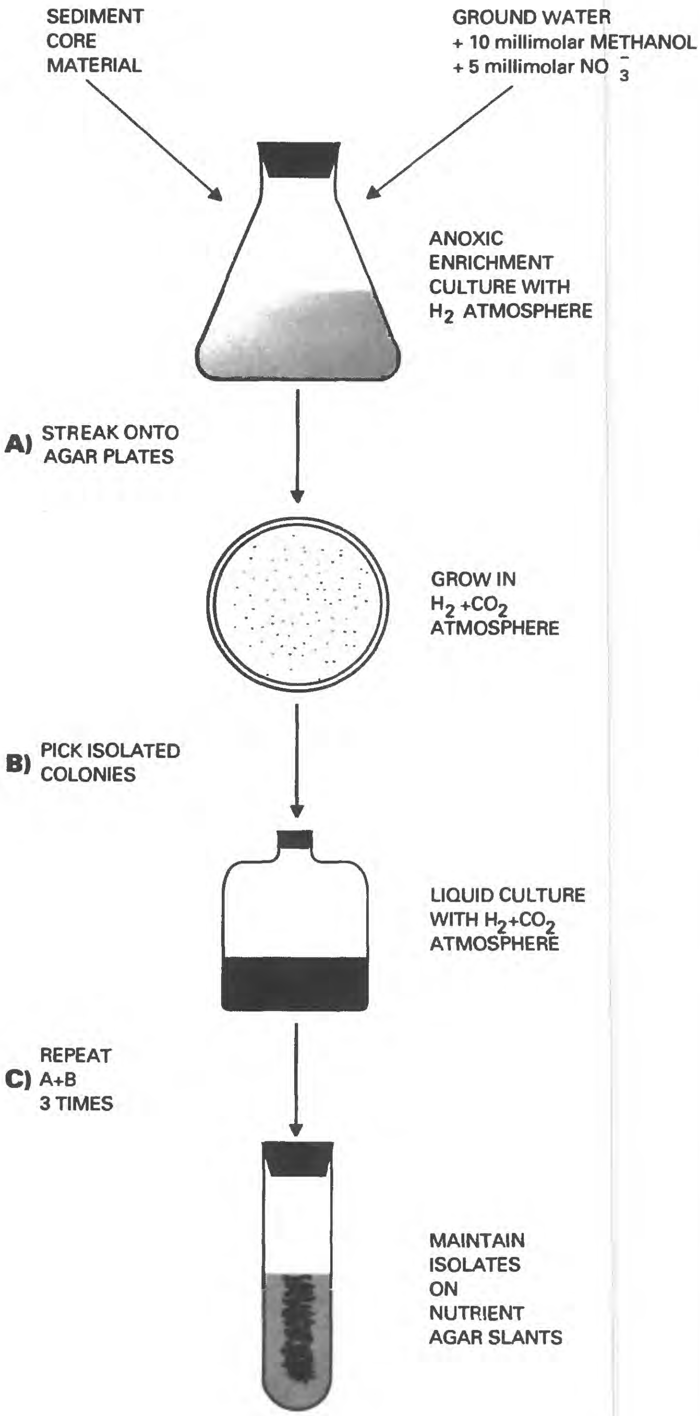


Figure 2. Time course of nitrate concentration (millimoles per liter) in sediment slurries when incubated at 32 degrees Celsius in flasks containing nitrogen gas in the headspace (endogenous) or nitrogen gas plus hydrogen gas. Slurries were composed of 75 grams sediment collected from site F347 (4.1 to 4.3 meters below the water table) in June 1990 and 150 milliliters of ground water from well F347M1-0.

Aerobic hydrogen oxidation by microorganisms that can also denitrify has been known for some time (Holt, 1984). However, virtually no information is available concerning anaerobic hydrogen oxidation by denitrification. Before this process can be exploited for bioremediation, the microorganisms responsible for this activity need to be isolated and characterized. Consequently, enrichment cultures were established by inoculating aquifer sediments from sites F347 and F473 into O_2-free ground water collected from the same site and supplemented with H_2, methanol, and nitrate as substrates (fig. 3). (Methanol was added in a parallel attempt to also grow methanol-oxidizing denitrifiers.) The enrichment cultures were incubated under anoxic conditions at 30 degrees Celsius. Pure cultures of hydrogen-oxidizing denitrifying bacteria were isolated from the enrichment cultures, using the isolation scheme depicted in figure 3. In all, a total of eight strains were isolated and designated as hydrogen- oxidizing denitrifiers (HOD). HOD 1-4 originated from site F473, whereas HOD 5-8 came from site F347.

All eight isolates were capable of autotrophic growth as denitrifiers, using H_2 and nitrate for energy requirements and fixing carbon dioxide for carbon. No organic carbon was present in the medium (fig. 3). Autotrophic denitrification by species such as *Thiobacillus denitrificans*, which couples the oxidation of reduced sulfur compounds to denitrification, is well known (Stanier and others, 1970). However, this appears to be one of the first reports of autotrophic growth by denitrifying bacteria with hydrogen as the electron donor. We later discovered that a laboratory strain of *Paracoccus denitrificans* was also capable of autotrophic growth on H_2 and nitrate. None of the isolates were obligate autotrophs nor obligate denitrifiers; all could grow aerobically on heterotrophic media. All were gram negative rods, some occurring singly and in pairs, whereas others grew in long chains (table 2). The cellular fatty acid profile for each of the isolates was compared to a library of fatty acid profiles for known strains of bacteria (table 3). Similarity indices indicated very strongly that isolates HOD 2 and HOD 8 were members of the genera *Hydrogenophaga* and *Methylobacterium*, respectively. For comparison, the similarity index for the known strain of *Paracoccus denitrificans* to the *Paracoccus* in the library was 0.84, which is considered a good match. The other isolates were identified with a lesser degree of confidence. For some, such as HOD 5 and HOD 6, there was no clear distinction between two different genera (table 3), whereas HOD 3 was very poorly matched and is probably unlike any of the organisms in the library. In these cases, the isolates will have to be identified by other techniques.

The ideal electron donor to use for bioremediation by denitrification in ground-water systems would (1) be innocuous, as would its oxidation product; (2) be a substrate that the indigenous population of denitrifiers could utilize; (3) also be a substrate that could fuel O_2 respiration if it were first necessary to consume background O_2; and (4) have a very limited utility for any nontargeted group of


SEDIMENT CORE MATERIAL
GROUND WATER
+ 10 millimolar METHANOL
+ 5 millimolar NO_3^-
ANOXIC ENRICHMENT CULTURE WITH H_2 ATMOSPHERE
A) STREAK ONTO AGAR PLATES
GROW IN H_2 +CO_2 ATMOSPHERE
B) PICK ISOLATED COLONIES
LIQUID CULTURE WITH H_2+CO_2 ATMOSPHERE
C) REPEAT A+B 3 TIMES
MAINTAIN ISOLATES ON NUTRIENT AGAR SLANTS

GROWTH MEDIUM	AMOUNT/LITER
$MgSO_4 \cdot 7H_20$	0.2 grams
$NaNH_4H PO_4 \cdot 4H_2O$	3.5 grams
$K_2 HPO_4$	5.0 grams
$KH_2 PO_4$	3.94 grams
$Na NO_3$	1.7 grams
TRACE ELEMENT SOLUTION	0.5 milliliters
0.1% RESAZURIN SOLUTION	2 milliliters
0.03% $Fe Cl_3$ SOLUTION	20 milliliters

GROWTH CONDITIONS	
pH	7.0
TEMPERATURE	30°Celsius
ANOXIC	

Figure 3. Flow diagram of isolation procedure used to obtain hydrogen-oxidizing denitrifying bacteria.

Table 2. *General characteristics of hydrogen-oxidizing denitrifying bacteria isolated from the denitrification zone of the Cape Cod contaminant plume*

Isolate	Gram reaction	Morphology	Aerobic growth on nutrient agar
HOD 1	-	Rods--singles and pairs	+
HOD 2	-	Rods--long chains	+
HOD 3	-	Rods--singles and pairs	+
HOD 4	-	Rods--singles	+
HOD 5	-	Rods--singles	+
HOD 6	-	Rods--long chains	+
HOD 7	-	Rods--singles	+
HOD 8	-	Rods--singles and pairs	+

microorganisms. Hydrogen appears to fit all of these requirements. As these results clearly demonstrate, the indigenous population of denitrifying bacteria in the Cape Cod aquifer can readily utilize hydrogen to consume contaminant nitrate. The reaction products, H_2O (the oxidation product of H_2) and N_2 (the reduction product of nitrate), are present in pristine ground water, whereas H_2 is not toxic in the low, solubility-limited concentrations that would be added to ground water. The oxidation of hydrogen will virtually be limited to the end step in a microbial food chain (the terminal electron-accepting process (Lovley and others, 1990)), which is denitrification in a nitrate-reducing zone. Thus, the addition of hydrogen would be much more oriented to the target microbial process (that is, denitrification) than would the addition of a general electron donor such as glucose. At least some of the hydrogen-oxidizing denitrifiers, such as the *Paracoccus denitrificans*, can also oxidize H_2 aerobically. This means that, given the common situation where O_2 and nitrate were both present, these organisms could utilize the added H_2 to first deplete the *in-situ* O_2, a prerequisite for denitrification, and then switch to denitrification to consume the nitrate that was present.

SUMMARY AND CONCLUSIONS

The stimulation of denitrification by the addition of hydrogen to remediate nitrate contamination in ground-water systems appears to be an approach that warrants further study. Hydrogen fits the criteria necessary to make it a good agent for this particular application and the isolation of ground-water denitrifying bacteria that can autotrophically oxidize hydrogen demonstrates that the process could take advantage of indigenous microorganisms. This is important because the need to add nonnative or genetically engineered organisms can be a distinct disadvantage for a bioremediation treatment. Before this particular bioremediation can be initiated, however, a detailed characterization of these hydrogen-oxidizing denitrifying bacteria is needed so that (1) the stoichiometry of the process can be carefully coupled to the extent of nitrate contamination and the rate of transport at a given site, and (2) the response of these microorganisms to the changes that will occur during remediation can be fully understood.

Table 3. *Tentative identification of hydrogen-oxidizing, denitrifying isolates using cellular fatty acid profiles*

Isolate	Genus match[1]	Similarity index[2]
HOD 1	*Hydrogenophaga*	0.25
HOD 2	*Hydrogenophaga*	.78
HOD 3	*Flavimonas*	.11
HOD 4	*Hydrogenophaga*	.35
HOD 5	*Chromobacterium*	.23
	Pseudomonas	.22
HOD 6	*Pseudomonas*	.40
	Hydrogenophaga	.38
HOD 7	*Methylobacterium*	.31
HOD 8	*Methylobacterium*	.92
ATCC 17741[3]	*Paracoccus*	.84

[1] Gas chromatographic analysis of methyl-ester derivatives of cellular fatty acids extracted with CH_3OH and NaOH from 24-hour cultures grown on trypticase soy-broth agar.

[2] Computed similarity fit to a library of cellular fatty acid profiles of known strains of bacteria. Theoretical range is 0-1.

[3] American Type Culture Collection strain of Paracoccus denitrificans.

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EFFECTS OF DENITRIFICATION ON NITROGEN GEOCHEMISTRY IN A NITRATE-CONTAMINATED SAND AND GRAVEL AQUIFER, CAPE COD, MASSACHUSETTS

By Richard L. Smith[1], Brian L. Howes[2], *and* John H. Duff[3]

ABSTRACT

A relatively narrow vertical zone (5-6 meters thick) of nitrate-containing ground water was identified using multilevel sampling devices within an unconfined sand and gravel aquifer located on Cape Cod, Massachusetts. The aquifer has been contaminated by surface disposal of treated sewage 0.3 kilometers upgradient from the study area. The nitrate zone was anoxic, contained high concentrations of nitrous oxide (16.5 micromolar), and coincided with a zone of active denitrification. Concentrations of nitrogen gas (N_2)*, the principal product of denitrification, were close to atmospheric equilibrium in uncontaminated ground water, but were significantly higher within the contaminant plume. The amount of excess* N_2 *was used to calculate the amount of nitrate reduced within a given transport interval. Denitrification resulted in an increase in the natural* $\delta^{15}N$ *of nitrate (from +13.6 to +42.0 per mil) and* N_2 *(+11.2 per mil per millimole per liter of* N_2 *produced) due to kinetic fractionation. The isotopic enrichment factor for in-situ denitrification was determined to be -13.9 per mil. These results demonstrate that denitrification can have a significant effect upon the geochemistry of ground water, but that closely spaced vertical sampling is necessary to study the process within aquifer environments.*

INTRODUCTION

On a global scale, nitrate is one of the most prevalent contaminants of ground-water systems. Nitrate originates from a variety of domestic, agricultural, and industrial practices. A great deal of attention has been devoted toward understanding processes that generate nitrate contamination in ground water, as well as those mechanisms that affect nitrate transport and dispersion within an aquifer. Nitrate is commonly found in ground water that is well oxygenated, and in that situation nitrate is relatively stable and mobile. However, as oxygen is consumed within an aquifer, it can become limiting to aerobic microbial respiration. When this happens, nitrate becomes the preferred electron acceptor and is subsequently reduced by nitrate-reducing microorganisms.

Denitrification is the reduction of nitrate to nitrogen gas and was found to be the predominant nitrate-reducing mechanism in a nitrate-contaminated sand and gravel aquifer (Smith and Duff, 1988). It is a dissimilatory, energy-generating process, which potentially can have a large effect on ground-water geochemistry. These effects include changes in speciation and isotopic composition of carbon and nitrogen-containing compounds that are substrates, products, and intermediates of the denitrification process. In general, few detailed studies have examined the effects of denitrification on the geochemistry of ground-water systems. This paper describes the results of a study to detail the effects of denitrification upon the geochemistry of inorganic nitrogen species in a nitrate-contaminated sand and gravel aquifer, in a region of the aquifer in which denitrification was the predominant terminal electron accepting process.

MATERIALS AND METHODS

The study was conducted in an unconfined sand and gravel aquifer located on Cape Cod, Mass. which has an extensive plume of contaminated ground water (fig 1.). The hydrogeology of the aquifer (LeBlanc, 1984), the nature of the contaminants within the plume (LeBlanc, 1984; Thurman and others, 1986; Barber and others, 1988; and Ceazan and others, 1989) and the effects of the plume on the microbial populations within the aquifer (Harvey and others, 1984; Smith, Harvey, and LeBlanc, 1991), have been described previously.

Ground-water samples were collected from a single site (well cluster F347, fig. 1) located in the center of the contaminant plume approximately 250 m (meters) downgradient from the contaminant source. Ground water was obtained from 5-centimeter inside-diameter observation wells with a submersible stainless-steel pump and from a multilevel sampling device with a peristaltic pump. Water samples were collected and assayed for nitrate, nitrous oxide, and nitrogen gas (Smith, Howes, and Duff, 1991).

Stable isotope analysis for ^{15}N was conducted with an isotope ratio mass spectrometer as described by Minagawa and others (1984) for nitrate and by Miyake and Wada (1967) for N_2. Results are expressed in units of per mil (‰) as

$$\delta^{15}N = ((R_{sample}/R_{standard}) - 1) \times 1{,}000\,, \qquad (1)$$

where R is $^{15}N/^{14}N$. The reference standard was atmospheric nitrogen.

RESULTS AND DISCUSSION

The sampling site chosen for this study contained relatively steep vertical gradients of specific conductance and dissolved oxygen (O_2) (Smith, Harvey, and LeBlanc, 1991). Specific conductance increased more than five-fold in the interval between 1.2 and 3.5 m below the water table (bwt) whereas O_2 decreased from 300 µM (micromolar) to less than 5 µM within the same interval. Nitrate concentrations increased dramatically within the same interval that specific conductance was increasing and O_2 was decreasing,

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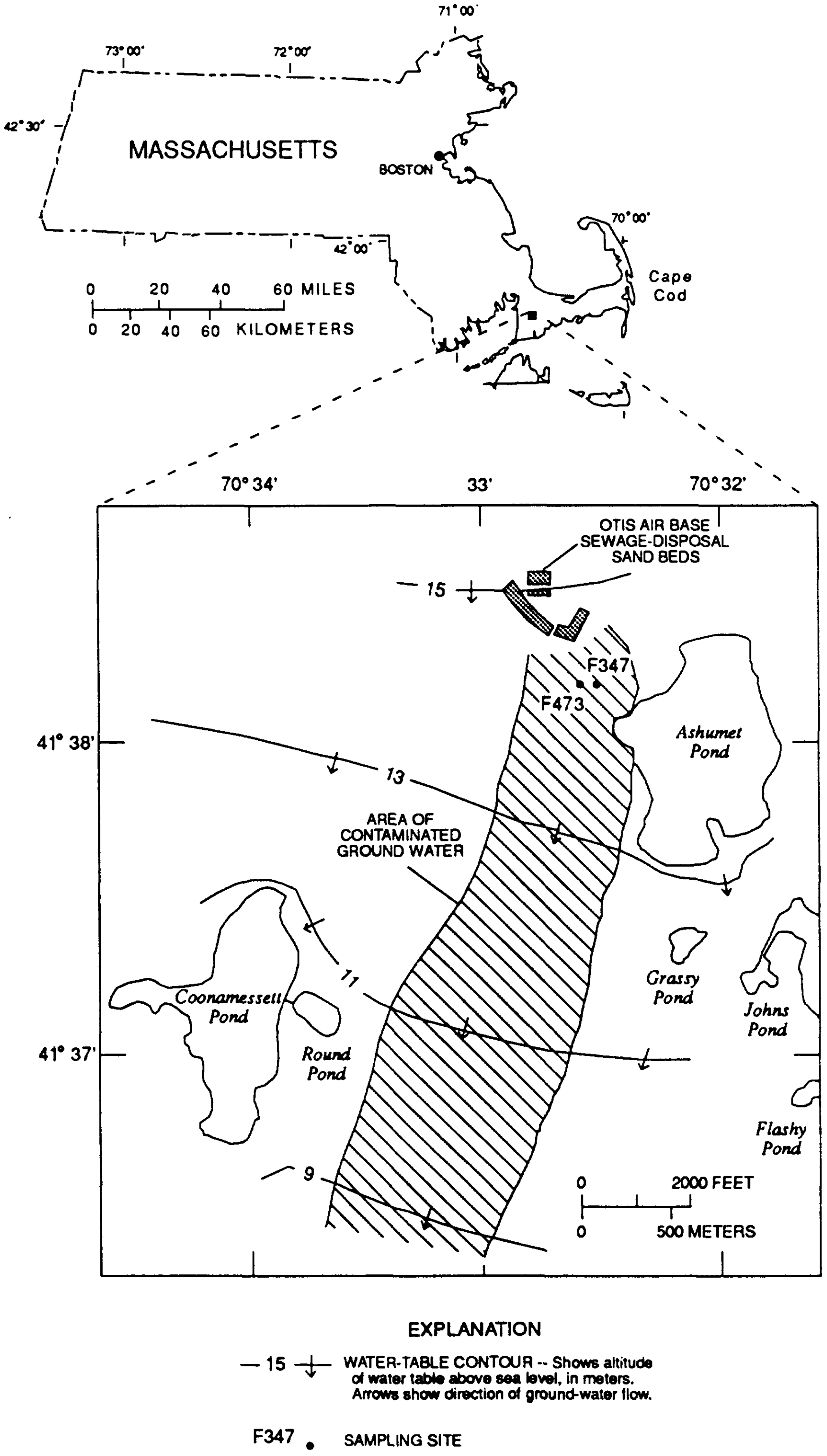
[2] Woods Hole Oceanographic Institution, Woods Hole, Mass.

[3] U.S. Geological Survey, Menlo Park, Calif.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F347 ● SAMPLING SITE

Figure 1. Ground-water site on Cape Cod, Massachusetts, showing the location of the contaminant plume and the well sites sampled for this study.

but nitrate concentrations subsequently decreased with depth to undetectable levels below 8 m bwt (fig. 2A). The peak nitrate concentration exceeded 800 µM. In addition, high nitrous oxide concentrations were associated with the lower part of the nitrate-containing zone. A peak nitrous oxide concentration of 16.5 µM was located 2.3 m below the nitrate peak (fig. 2).

The particular set of geochemical conditions found at well F347 strongly suggest that denitrification was occurring in the subsurface at this site. The presence of nitrate and low O_2 concentrations are prerequisites for denitrification in most situations, and nitrous oxide is an intermediate product of the denitrification process. In an earlier study using sediment slurry incubations, we were able to demonstrate that denitrification was occurring within the nitrate-containing zone at well F347 (Smith and others, 1989). The activity was limited to a depth interval between 1.2 and 8.1 m bwt, which was virtually the nitrate-containing interval; the peak rate of denitrification was 0.25 nanomole N reduced per cubic centimeter per day and was located at the same depth as the nitrate maximum.

The ^{15}N content of nitrate at site F347 changed significantly with depth, particularly within the denitrifying zone (fig. 2). The δ^{15}N of nitrate in the shallowest part of the nitrate zone (+11.3 ‰) was similar to that of the sewage effluent (+13.6 ‰). These values fall within the range of nitrogen isotope values (δ^{15}N +10 to +20 ‰) reported for nitrate originating from animal and human waste (Kreitler, 1979; Heaton, 1986). However, nitrate became progressively enriched in ^{15}N with depth at F347, such that the δ^{15}N at the bottom of the nitrate-containing zone was +42.0 ‰. This is one of the heaviest nitrate values ever reported for ground water and strongly indicates that the nitrate at F347 is being subjected to kinetic isotopic fractionation by denitrification (Letolle, 1980).

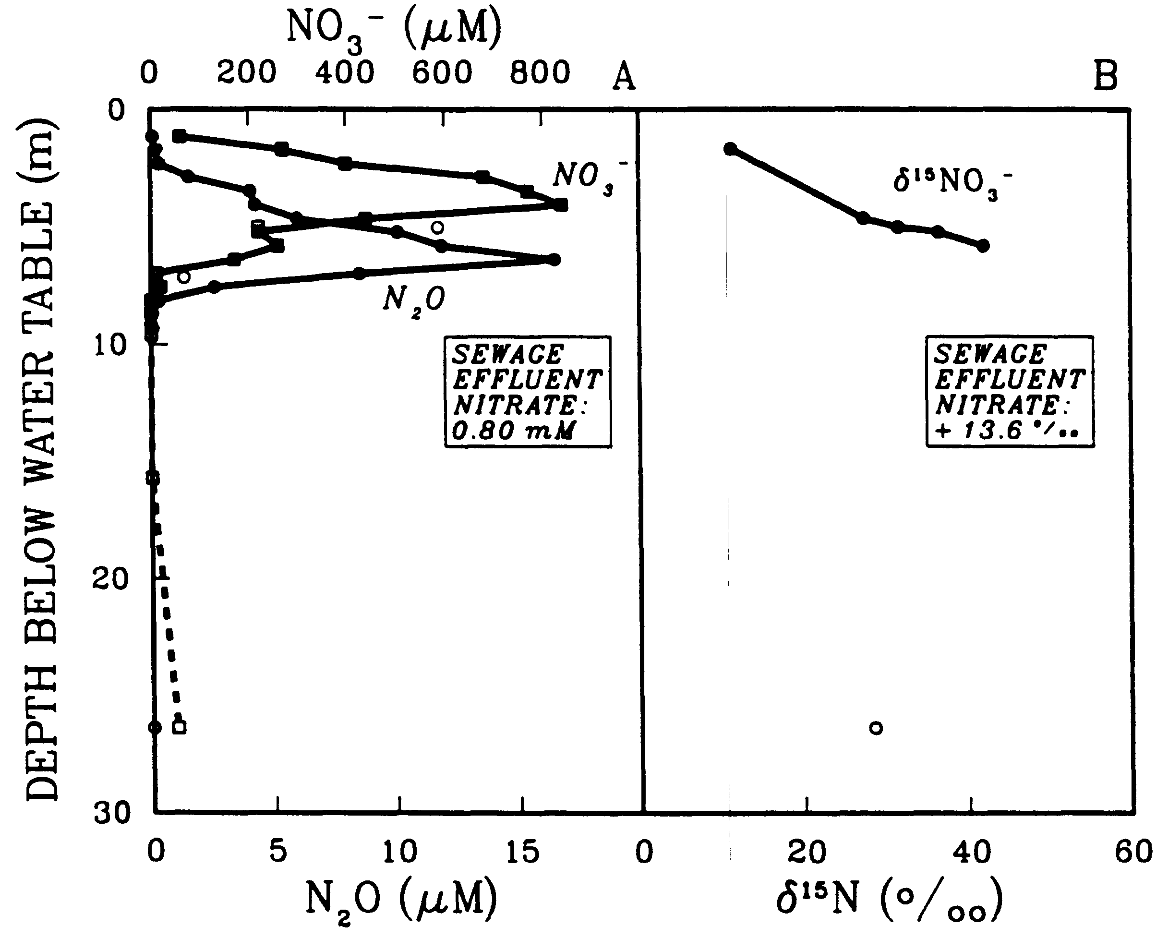

Figure 2. Vertical depth profile (meters below water table) of (A) nitrate and nitrous oxide concentrations (micromolar) and (B) δ^{15}N nitrate (per mil) at site F347 in October 1988. Closed symbols are samples collected from the multilevel sampler, open symbols are samples collected from monitoring wells.

Concentrations of N_2, the principal end product of denitrification, were near atmospheric equilibrium (0.64 mM (millimolar) N_2, at 1 atmosphere and 10 °C (degrees Celsius)) in the shallowest part of the aquifer at F347, then increased substantially with depth within the nitrate-containing zone, to a generally consistent concentration of 1.2 μM in the core of the contaminant plume (fig. 3A). N_2 concentrations at a comparable depth (14.5 m bwt) at an uncontaminated site upgradient from the sewage-disposal facility were only 0.78 μM. Although denitrification did not occur at F347 below 8 m bwt, it was occurring at greater depths upgradient from F347 (Smith and Duff, 1988), accounting for the elevated N_2 concentrations at F347 below a depth of 8 m. Total combined inorganic N within the contaminant plume is sufficient to preclude N_2-fixation (Brill, 1975), which means that the excess N_2 at any given depth at F347 can be used to calculate the amount of nitrate reduced by denitrification within the transport interval. This amounted to approximately 1.2 millimoles N_2-N in the core of the contaminant plume in October 1988. Dissolved N_2 concentrations change somewhat at F347 temporally, which might be expected inasmuch as the effluent nitrate concentration is variable. Vogel and others (1981) used a similar approach to correlate the amount of nitrate disappearing to the amount of excess N_2 produced along a ground-water flow path in the Kalahari Desert, but a flow path with a much different time scale. In that case, it required 14,000 years to completely reduce 1.5 μM nitrate to N_2.

In this study and in the Kalahari study, the production of N_2 by denitrification was evident in the isotopic composition of the N_2 dissolved in ground water. The $\delta^{15}N$ content of atmospheric N_2 is 0, by definition, with a small fractionation occurring (+0.8 to +0.9 ‰) for dissolved N_2 in equilibrium with the atmosphere (Letolle, 1980). The $\delta^{15}N$ content of N_2 in the shallowest well at F347, which was unaffected by the contaminant plume or by denitrification, was +0.1 ‰ (fig. 3B). The natural abundance of ^{15}N in N_2 increased with depth in the contaminant plume at F347 through the nitrate-containing zone, reaching peak values of +4.5 to +5.5 ‰ in the center of the plume (7.2-15.7 m bwt). Upgradient from the contaminant plume, the $\delta^{15}N$-N_2 at a depth of 14.5 m bwt was -0.7 ‰. The enrichment at F347 was due to the production of N_2 by denitrification from the contaminant nitrate, which was significantly heavier than the background N_2 (fig. 2B). Initially the reduction would result

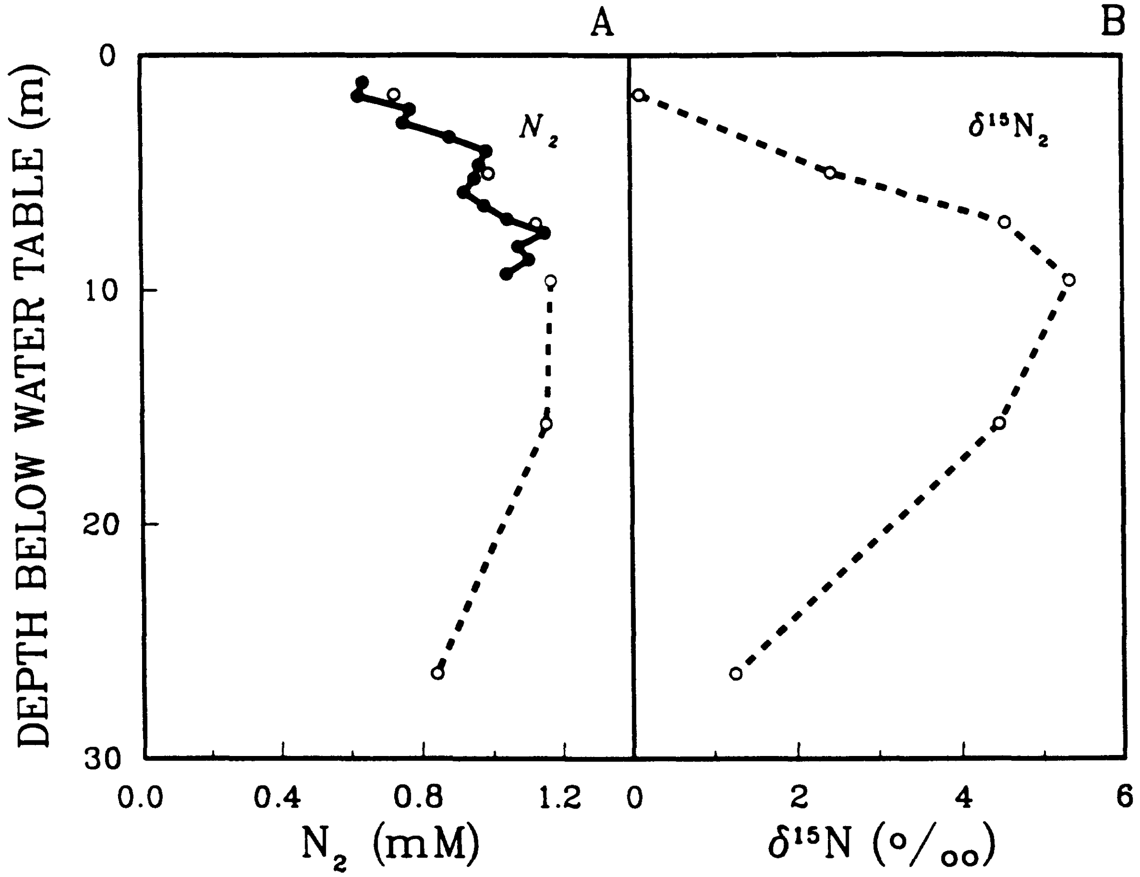

Figure 3. Vertical depth profile (meters below water table) of (A) dissolved N_2 concentration (millimolar) and (B) $\delta^{15}N$ N_2 (per mil) at site F347 in October 1988. Closed symbols are samples collected from the multilevel sampler, open symbols are samples collected from observation wells.

in a fractionation of ^{15}N between substrate and product. However, for those cases where the reaction has gone to completion (such as in the center of the plume at F347), the isotopic content of the N_2 produced will be identical to that of the original substrate (Mariotti and others, 1988). Then a simple mass balance can be calculated using the equation

$$(\delta^{15}N_2)_f = (\delta^{15}N_2)_i\, C_i/C_f + (\delta^{15}N_2)_d\, C_d/C_f \qquad (2)$$

where i and f refer to the initial and final conditions and d refers to the N_2 produced by denitrification. At 9.6 m bwt, the N_2 concentration was 1.17 mM; this represents an increase of 0.44 mM (60.1 percent) above the N_2 content of the 1.7 m sample (fig. 3). The $\delta^{15}N$ of that excess N_2 at a depth of 9.6 m bwt should be the same as that of the effluent nitrate (+13.6 ‰). Thus, because of denitrification, the $\delta^{15}N$ value of the 9.6 m deep sample should have increased to a calculated value of +5.2 ‰, which agrees well with the measured value of +5.3 ‰ (fig. 3B). This close agreement indicates that the sampling methodology used to determine the isotopic composition of N_2 dissolved in ground water did not introduce significant error and it suggests that there was no other nitrate-consuming mechanism of any consequence occurring within this region of the aquifer.

The isotopic fractionation that occurs during denitrification can be described as if the process were a single step unidirectional reaction (Mariotti and others, 1981; 1988) that results in the progressive enrichment of the ^{15}N content of the nitrate. The isotopic abundance of the nitrate at some time, t, in the reaction can be described by

$$\delta_t = \delta_{t=0} + \varepsilon \ln [NO_3]_t/[NO_3]_{t=0}, \qquad (3)$$

where ε is the isotopic enrichment factor (‰) of the reaction and $[NO_3]$ is the nitrate concentration at time t and time t = 0. ε is related to the fractionation factor, α, by $\varepsilon = (\alpha-1)1{,}000$. Therefore, as the nitrate is reduced, there should be a linear relation between the isotopic content of the nitrate and the

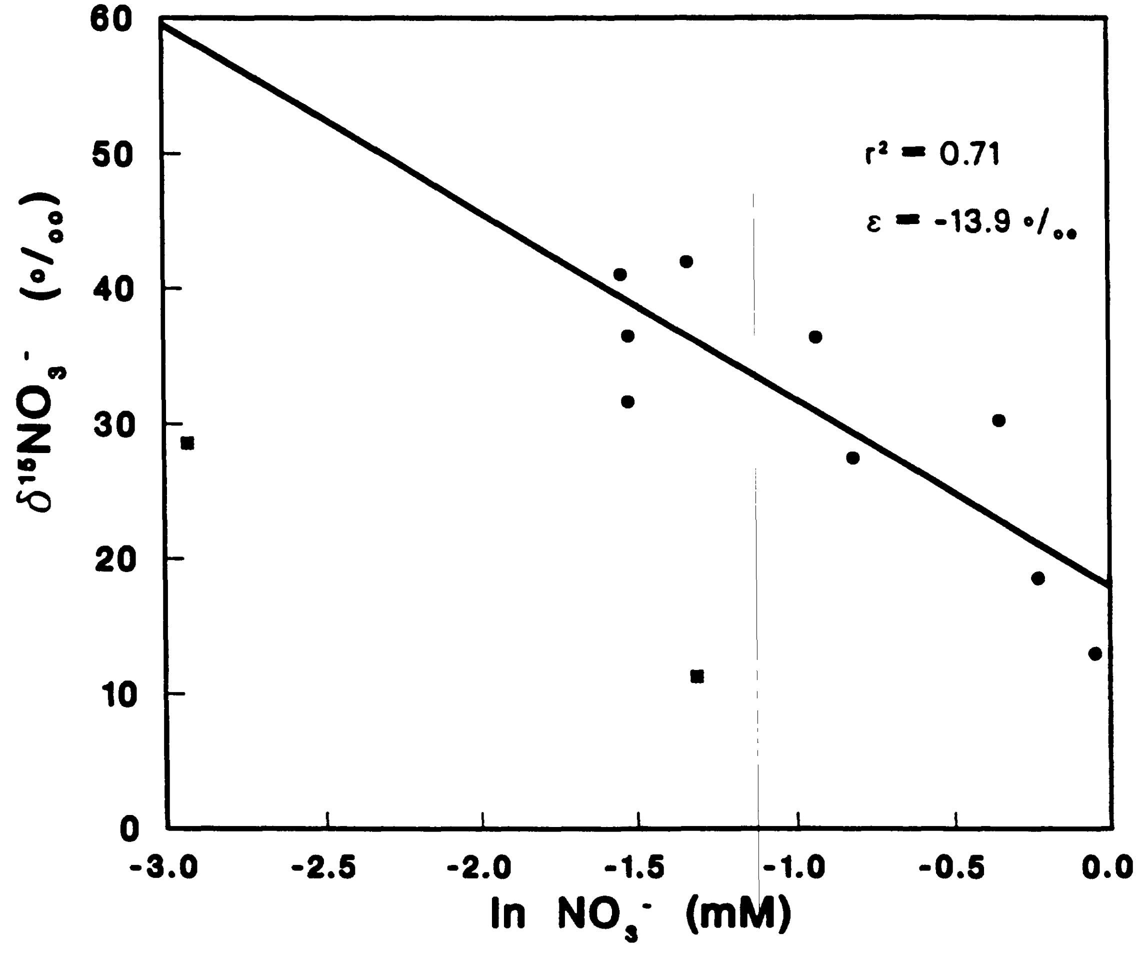

Figure 4. Relation between the ^{15}N composition of nitrate (per mil) and the natural logarithm of the nitrate concentration (millimolar) for samples obtained from well site F347 in October 1988 and well site F473 in October 1989. Circled are samples collected from the zone of denitrification, squares are samples where denitrification was not occurring. The line is a best-fit linear regression of the circles.

natural log of the nitrate concentration. This principle was used by Mariotti and others (1988) to demonstrate the occurrence of denitrification in nitrate-contaminated ground water in northern France. In the present study, a linear relation between the $\delta^{15}N$ value and the natural log of the nitrate concentration was also found for ground-water samples taken from the denitrification zone at two different sites (fig. 4). Nitrate-containing samples collected above and below the denitrification zone did not fit the relation. The isotopic enrichment factor for denitrification (ε is the slope of the line in fig. 4) was -13.9 ‰ (standard error = 3.3 ‰). This value lies midrange between enrichment factors reported for denitrification in ground waters in France, -4.7 to -5.0 ‰ (Mariotti and others, 1988), -25 to -29 ‰ for soils (Mariotti and others, 1981), -30 ‰ for an aquifer in the Kalahari (Vogel and others, 1981; Heaton, 1986), and -30 to -40 ‰ in an oceanic environment (Cline and Kaplan, 1975).

There was also a linear relation between the groundwater N_2 concentration and the ^{15}N content of the N_2 (fig. 5). The slope of this line indicated that ^{15}N increased by 11.2 ‰ mM^{-1} N_2 (standard error = 0.9). The data in fig. 5 come from depth intervals in which denitrification has gone to completion or does not occur. Because denitrification is the only process that was affecting ground water N_2 concentrations, this relation is a simple one and is linear under these conditions. This should not be the case within the nitrate-containing interval because of isotopic fractionation between nitrate and N_2 by denitrification. However, the physical constraints imposed by this narrow vertical interval precluded collection of appropriate water samples for delineating the relation within the active zone of denitrification.

Studies of microbial processes in a natural environment need to account for the spatial heterogeneity of the physical and geochemical properties of that environment. This study and others (Ronen and others, 1987; Molz and Widdowson, 1988; Smith, Harvey, and LeBlanc, 1991) have demonstrated that vertical geochemical gradients are common in ground water systems and that these gradients can exist in vertical intervals that are very narrow relative to the thickness of the aquifer and to the length of well screens that typically exceed 1 m. Locating and characterizing the steepness of these gradients are

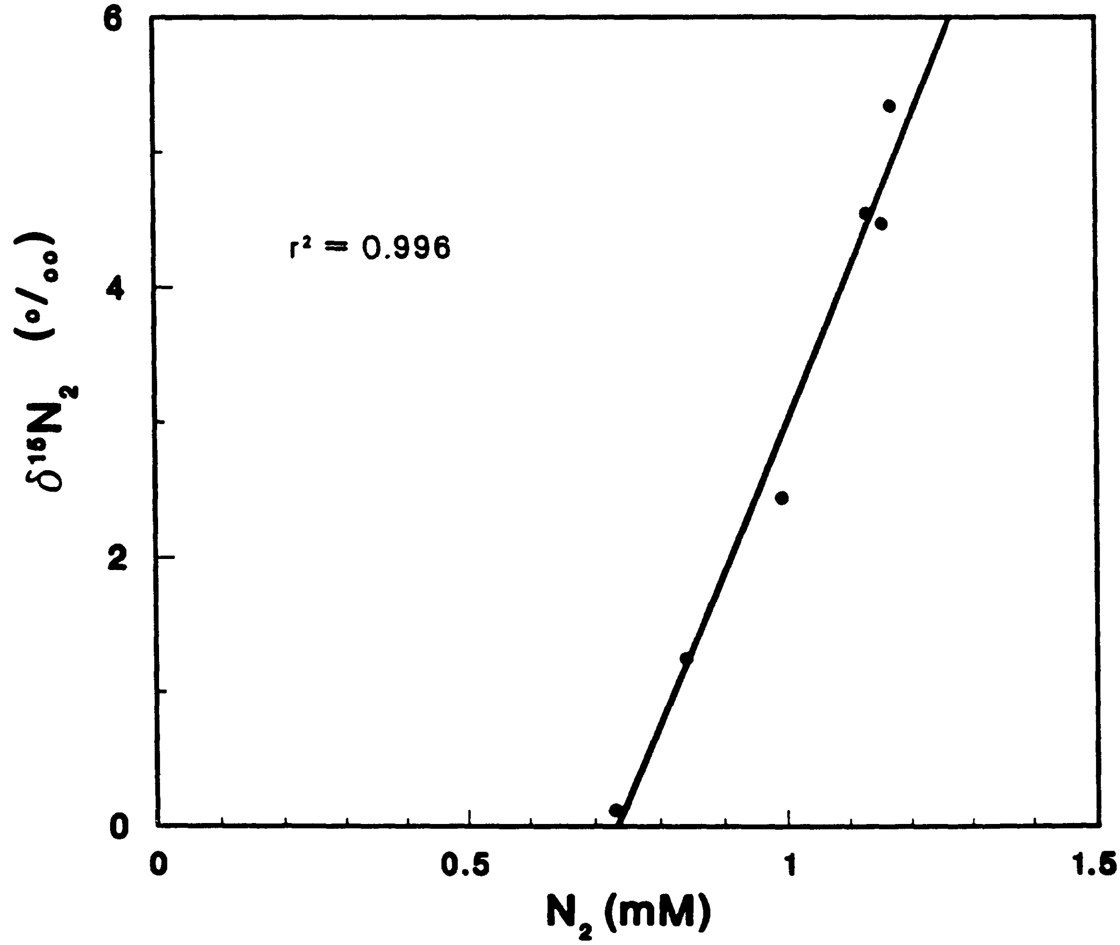

Figure 5. Relation of the ^{15}N composition of dissolved N_2 (per mil) and the N_2 concentration millimolar) for samples obtained from well site F347 in October 1988. The line is a best-fit linear regression.

essential to understanding the relation between the geochemical and the microbiological processes occurring within the aquifer, as was the case for this study on denitrification in ground water.

SUMMARY

Denitrification, the microbial reduction of nitrate to molecular nitrogen, altered the geochemistry of nitrate-contaminated ground water on Cape Cod. The process consumed nitrate and produced nitrous oxide and N_2 in amounts that were in excess of simple equilibrium with the atmosphere. Because there were no other sources or sinks for N_2 within the denitrifying zone, the amount of excess N_2 could be used to calculate the amount of nitrate reduced by denitrification within a given transport interval. Denitrification also affected the $\delta^{15}N$ values of nitrate and N_2 by kinetic fractionation, resulting in a significant increase in the ^{15}N content of the residual nitrate. The isotopic enrichment factor for denitrification was determined to be -13.9 ‰. These findings (1) further demonstrate that denitrification can be a significant mechanism for nitrogen (and therefore carbon) mineralization in ground-water systems; (2) will serve as a useful tool for predicting where denitrification might be occurring in ground water on the basis of geochemical evidence; and (3) help to improve characterization of the overall nature of denitrification in natural environments.

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DEOXYRIBONUCLEIC ACID DISTRIBUTIONS AND RECOVERY IN A SAND AND GRAVEL AQUIFER ON CAPE COD, MASSACHUSETTS

By David W. Metge[1] *and* Ronald W. Harvey[1]

ABSTRACT

A fluorometric-deoxyribonucleic acid (DNA) assay was evaluated for use in microbiological studies of sewage-contaminated aquifer sediments. Variations in quantity and in solute:solid and intracellular:extracellular partitioning of DNA were estimated in a 5-kilometer-long contaminant plume within a sand and gravel aquifer on Cape Cod, Massachusetts. These variations were correlated with ground-water chemistry and proximity to the source of contamination (on-land outfall for secondarily treated sewage). Most DNA (up to 99 percent) in the aquifer was particle-associated, and a surprisingly large fraction (up to 50 percent) of the DNA in contaminated aquifer sediments was extracellular and adsorbed. At some locations near the source of contamination, substantial fractions of porewater DNA were found to be associated with the protozoan-size fraction. Per-cell DNA content differed substantially among samples (2 to 14 and 2 to 20 femtograms per cell for adherent and free-living bacteria, respectively) and decreased with increasing distance from the contaminant source. In a separate study, an unidentified Pseudomonad bacterium isolated from the contaminant plume and grown in pure culture exhibited a fivefold variation in per-cell DNA content in response to a tenfold difference in growth rate. Several biotic and physical factors were found to affect the accuracy of the DNA assay for providing quantitative information involving bacterial distributions within aquifer sediments. Recovery of sediment-associated DNA depended on desorption conditions, mineralogy (sediment silt content), experimental protocol used, and bacterial lysis methodology.

INTRODUCTION

Changes in aquifer microbial community structures and biomass are one of the more important indicators of ground-water pollution (Gunnison, 1986). In the last several years, researchers have estimated microbial abundance by total adenylates, deoxyribonucleic acid (DNA), acridine orange direct counts (AODC), fluorescent antibody, and phospholipid analyses. Karl (1986) provides a good review of the different techniques and their inherent advantages and disadvantages with regard to use and interpretation. Multidisciplinary research on contaminated ground water and subsurface environments is being undertaken in several areas in the United States. One such region is a shallow, sandy aquifer on Cape Cod, Mass. The research effort on contaminated ground water is detailed in LeBlanc (1984).

The use of DNA in environmental studies has grown significantly in the last few years. Examples include genetic-probe analyses to detect the presence of genetically engineered sequences and useful proteins of environmental concern, such as key enzymes involved in the breakdown of organic-contaminants (Ogunseitan and others, 1987). DNA analyses allow researchers flexibility in monitoring microbial communities at the genetic level without requiring culturing of the microorganisms (Steffan and others, 1988). The highly refractory nature of liberated DNA may cause it to persist in ground-water habitats where it may be utilized as a source of nucleic acids and nitrogen in nutrient-poor environments, and to effect genetic transformations of other microbes. DNA has been used to estimate microbial biomass in estuaries (Paul and Myers, 1982), freshwater (McCoy and Olson, 1985), and ground water (Metge and Harvey, 1989).

Our objectives were to devise methodologies for estimating DNA content in sediments of an aquifer on Cape Cod. We previously had estimated levels of DNA partitioning between solute and solution at five locations within the contaminant plume and found that DNA was correlated to bacterial abundance in ground water and sediments (Metge and Harvey, 1989). The focus of the study was to (1) define DNA partitioning in contaminated aquifer sediments, (2) estimate contributions from the protozoan community to the overall DNA pool, (3) compare results of per cell levels of DNA with isolates cultured in the laboratory, (4) examine variations in per-cell DNA content with growth rate in laboratory cultures, (5) determine whether DNA-related estimates of microbial biomass correlated with cell numbers, and (6) optimize recovery of DNA from sediments.

MATERIALS AND METHODS

Study Site

The study site is a sand and gravel aquifer located on Cape Cod, Mass. Disposal of secondarily treated sewage in infiltration beds since 1936 has resulted in an extensive plume of contaminated ground water.

Sample collection and filtration

Pore waters and sediments were collected for bacterial enumeration and DNA analyses along a longitudinal transect of the contaminant plume shown in figure 1. Ground water was sampled from a network of observation wells that were pumped until specific conductance and temperature had stabilized. Replicate ground-water samples used to estimate DNA concentrations were vacuum filtered at 390 mm (millimeters) mercury to minimize premature lysis of cells, using a sampling manifold with 25-mm-diameter, 8-µm (micrometer)-pore-size backing and 0.22- or 0.10-µm pore-size membrane filters. Size fractionation and partitioning of

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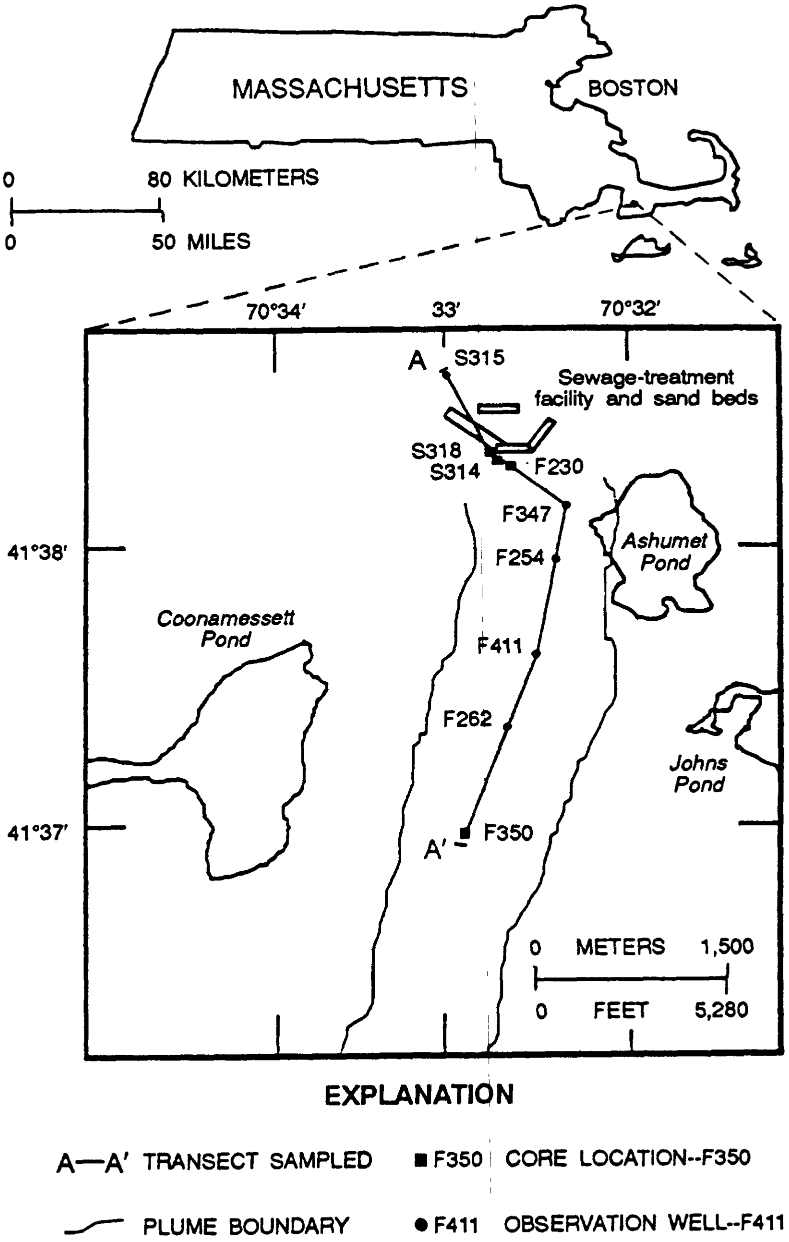
ground water was done using an in-line filtering apparatus under vacuum filtration. Either an 8- or a 5-µm pore-size membrane filter was used to trap the larger fraction (referred herein as the eukaryotic fraction). The filtrate was then filtered with a 0.22- or 0.1-m pore-size membrane filter to trap the fraction smaller than 5 µm (referred herein as the prokaryotic fraction). Sediment samples were collected by a wireline piston-coring device that was used with a hollow-stem auger drill.

Analyses

Bacteria were enumerated using the AODC method modified for use with Cape Cod ground water by Harvey and others (1984). Modifications were made to published methods for fluorometric determination of DNA concentrations in cell lysates by using a DNA-specific fluorochrome, Hoechst 33258[2] (Paul and Myers, 1982).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BOSTON
0 80 KILOMETERS
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70°34'
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41°37'
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S315
Sewage-treatment facility and sand beds
S318
S314
F230
F347
F254
F411
F262
F350
A'
Ashumet Pond
Coonamessett Pond
Johns Pond
0 METERS 1,500
0 FEET 5,280
EXPLANATION
A—A' TRANSECT SAMPLED
■ F350 CORE LOCATION--F350
PLUME BOUNDARY
● F411 OBSERVATION WELL--F411

Figure 1. Location of study site on Cape Cod, Massachusetts, transect, and approximate plume boundary.

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[2] The use of brand or trade names in this paper is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

Filter residues from processed ground-water samples were placed in sterile autoclaved borosilicate scintillation vials with 2.0 mL (milliliters) solution of 10 mM (millimolar) tris-(hydroxy-methyl)-aminomethane (TRIS), 100 mM salt (NaCl), 1 mM, pH 7.5 ethylene-diamine-tetraacetic acid (EDTA) buffer (abbreviated as STE) and kept at -20 °C (degrees Celsius) until analysis. Filter blanks were prepared by filtering 100 mL of distilled water through a 0.2- or 5-µm pore-size membrane filter, spiking the filter with 0.0 to 0.6-micrograms per milliliter DNA and then adding lytic agents to 2 mL. Nonspecific fluorescence was measured. Recovery of DNA from the filters was estimated and corrected for in final DNA concentration calculations.

DNA content of aquifer sediments was estimated by using a modification of methods outlined in Lorenz and Wackernagel (1987), Ogram and others (1987), Steffan and others (1988), and Metge and Harvey (1989). DNA desorption was investigated by using different experimental buffer systems of salt-sodium citrate (SSC), TRIS-EDTA (TE), and phosphate. Recovery and desorption of DNA from sediments was examined from pH 2.00 to 12.00, and over time. Bacterial lysis efficiency was checked by direct epifluorescence microscopic observations of bacterial lysates. DNA recovery was estimated using spike and recovery analysis of organically stripped sediments using the sodium hydroxide stripping method of Harvey and others (1984).

A gram negative Pseudomonad bacterium, designated Ps-1, was isolated from a well 0.30 km (kilometers) downgradient from the effluent-discharge beds. Cultures were grown in half-strength nutrient broth amended with 10-percent ground water. Growth rates for the culture were determined. DNA samples (1-5 mL) were filtered using 25-mm diameter 0.2-µm pore-size membrane filters. Appropriate modifications were made in lysing cells to accommodate greater biomass. Additionally, DNA was purified by hydroxylapatite liquid chromatography before fluorometric assay according to the method of Ogram and others (1987). We used *Escherichia coli* K-12 and *Bacillus subtilis* ATCC 6051 cultures in log phase for checks of the laboratory DNA assay.

RESULTS AND DISCUSSION

Bacterial abundance in porewater of the contaminant plume decreased with distance from the contaminant source. The maximum and minimum of 27.2 and 0.15 ng/mL (nanograms per milliliter) DNA concentrations coincided with the maximum and minimum cell abundance of 4.03×10^6 and 2.43×10^5 cells per mL at 260 and 3,030 m (meters) downgradient, respectively. A linear regression analysis of the relation of DNA concentrations to bacterial abundance in ground water was highly correlated ($r=0.94$, $p \leq 0.001$). We found a similar per-cell DNA content as that reported by Paul and Myers (1982) (10 nanograms DNA per 10^6 cells). Thus, it seemed reasonable to calculate bacterial numbers from the measured prokaryotic DNA concentrations obtained during our study.

For all but one of the nine studied sites along the transect (shown in fig. 1), most of the DNA was associated with the bacterial size fraction. The largest eukaryotic DNA pool of 4.45 ng/mL was located at well F230, a site 180 m downgradient from the contaminant source and at 17.7-m depth where a large population of amoebae and zooflagellates were observed (N.E. Kinner, University of New Hampshire, oral commun., 1988). There was no measurable eukaryotic contribution to the DNA pool at well F411 at a depth of 19.8 m, 1,370 m downgradient from the contamination source. These two sampling sites represented extremes of eukaryotic DNA concentration within the region studied. Eukaryotic DNA accounted for 54.8 percent of the total DNA found at well F230, 0.18 km from the source and at a depth of 17.7 m. However, at most sites, eukaryotes contributed less than 20 percent of the total porewater DNA. Prokaryotic DNA from an uncontaminated site, well S315, located approximately 500 m upgradient from the contaminant source and at a depth of 32 m, was 0.145 ng/mL--a concentration an order of magnitude lower than the lowest concentration found in the contaminant plume, 2.37 ng/mL at well F262, at a depth of 19.8 m. No measurable eukaryotic DNA was found at well S315.

Per-cell levels of bacterial DNA differed among ground-water samples collected along the transect. These values ranged from a high of 20.7 fg/cell (femtograms per cell) 730 m downgradient to a low of 6.5 fg/cell, 1,860 m downgradient and within the plume. There was no clear relation between per cell DNA content and distance from the contaminant source. The mean DNA per-cell value was 6.7 ± 3.6 fg for the nine sampling sites. Paul and Carlson (1984) reported per-cell DNA masses of 6 to more than 20 fg/cell, with an average of about 10 fg/cell--results similar to our data. No particular reason can be given for the large per-cell DNA value at 730 m from the contaminant source at well F254. Brooks and Smith (1989) found that the microbial-community energy charge was quite low throughout the same transect. Bacterial DNA in estuarine systems is reported to range from 6.6 to 14 fg/cell (Paul and Carlson, 1984) and, in oceanic environments, from 2.1 to 11.2 fg/cell (Paul and others, 1988).

An isolate from the contaminant plume (designated Ps-1) was used to assess how DNA values changed during a growth curve experiment. The growth rate (μ measured in reciprocal hours) was calculated as the natural logarithm of 2 divided by g, the time required for cultured bacteria to double in number--that is, $\mu=\ln 2/g$. Per-cell DNA content for a pure culture of Ps-1 varied significantly in a batch culture, decreasing more than fivefold from 11.3 fg/cell (at $\mu=0.463$/hr) to 2.0 fg/cell (at $\mu=0.0106$/hr) seen in figure 2. Previously, cellular DNA estimates for the isolate in stationary phase, when grown in unamended culture media, were about 4.9 (± 1.5) fg/cell (unpublished data on file in the Boulder, Colo., office of the U.S. Geological Survey); experiments with log phase cultures of *Escherichia coli* K-12 and *Bacillus subtilis* resulted in per cell DNA levels of 9.7 (± 1.3) and 11.6 (± 6.7) fg/cell, respectively. Reported estimates of cellular DNA for bacteria isolated from other freshwater systems range from 6.0 to 27 fg/cell (McCoy and Olson, 1985). Harvey and George (1987) found that the growth rates (μ) of porewater bacteria are quite low, ranging from 0.001/hr to 0.047/hr, in a similar longitudinal transect. Thus, the range of bacterial growth rates estimated in the field differed significantly from the growth experiment

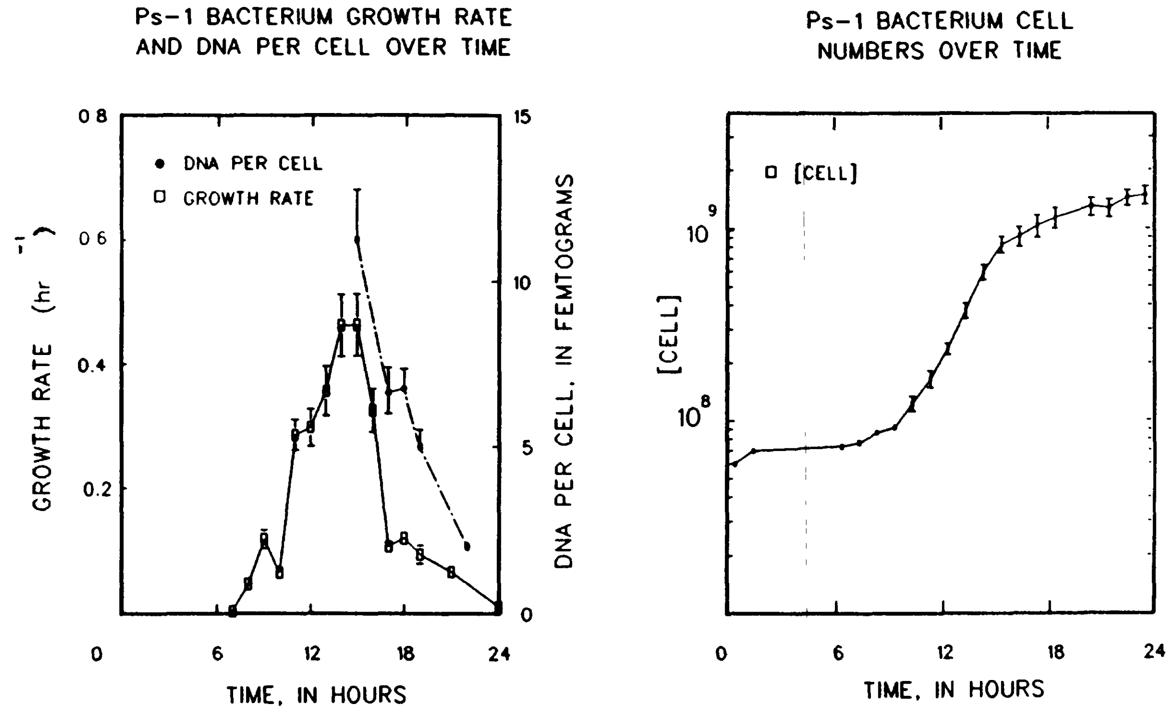

Figure 2. Changes in growth rate of Ps-1 bacterium grown in half strength nutrient broth for 24 hours.

performed in the laboratory, which somewhat complicates the interpretation of laboratory results. Nevertheless, per-cell DNA content changes with growth rate and may need to be taken into account when using DNA to estimate bacterial abundance across nutrient gradients.

We found that slightly alkaline conditions were necessary for maximum recovery of DNA from aquifer sediments; recovery could be further maximized by changing the type of buffer used. Table 1 summarizes DNA recoveries from DNA-spiked aquifer sediments that had been previously chemically stripped of microorganisms and other sorbed organics. The greatest recovery was found when a combination of TRIS-EDTA and dibasic phosphate buffers were used over a period of 20 hours. The lowest recovery was found when sodium chloride-sodium citrate was used, yielding a recovery of only 1.5 percent.

Table 1. *DNA recoveries using different buffer protocols at alkaline pH (8.5 to 9.0) [%, percent; percentages are the amount of DNA spike recovered from sediments]*

Buffer	SSC[1]	Phosphate[2]	SSC[3] TE	TE[4]	SSC[5] Phosphate	TE[6] Phosphate	TE[7] Phosphate
Recovery	1.5%	24.6%	28.4%	36.1%	76.3%	81.9%	95.1%

[1] NaCl-sodium citrate (100% 0.154 M NaCl, 15 mM trisodium citrate, pH 7.0)

[2] Phosphate (100% 0.15 M Na_2HPO_4)

[3] NaCl-sodium citrate/TE (25% SSC, 75% 20 mM TRIS, 200 mM EDTA, pH 6.5)

[4] TRIS-EDTA (100% TE)

[5] NaCl-sodium citrate/phosphate (25% SSC, 75% phosphate)

[6] TRIS-EDTA/phosphate (25% TE, 75% phosphate)

[7] TRIS-EDTA/phosphate (25% TE, 75% phosphate, desorption time--20 hours)

All other desorption treatments were for ~ 2 hours; sediments taken from sites 0.05-3.03 km from the sewage plant.

Attached (sediment-bound) and unattached (free-living) microbial communities were sampled in this study. Harvey and others (1984) found that particle-associated microorganisms predominate. The desorption of DNA from spiked sediments indicated that the presence of buffer containing phosphate and low-ionic-strength salt over an extended time gave the greatest DNA recovery. The recoveries of DNA in high-ionic-strength media (>0.15 molar sodium (Na^+)) were low and have been documented elsewhere (Steffan and others, 1988). Lorenz and Wackernagel (1987) suggested that the adsorption of DNA to marine sands was rapid and depended on ionic conditions, such as the concentration of Na^+.

The results of DNA partitioning between solid surfaces and adherent and free-living bacteria and protozoa within the aquifer transect studied are shown in figure 3. They indicate that the proportion of free-living bacterial DNA in the total DNA pool decreases in the downgradient direction. Adsorbed extracellular DNA varied over the length of the plume and constituted more than 50 percent of the total in at least one sample. In this study we found that 85 to 99 percent of the DNA is associated with aquifer sediments. This is not a surprising result inasmuch as other researchers have found that extracellular DNA can

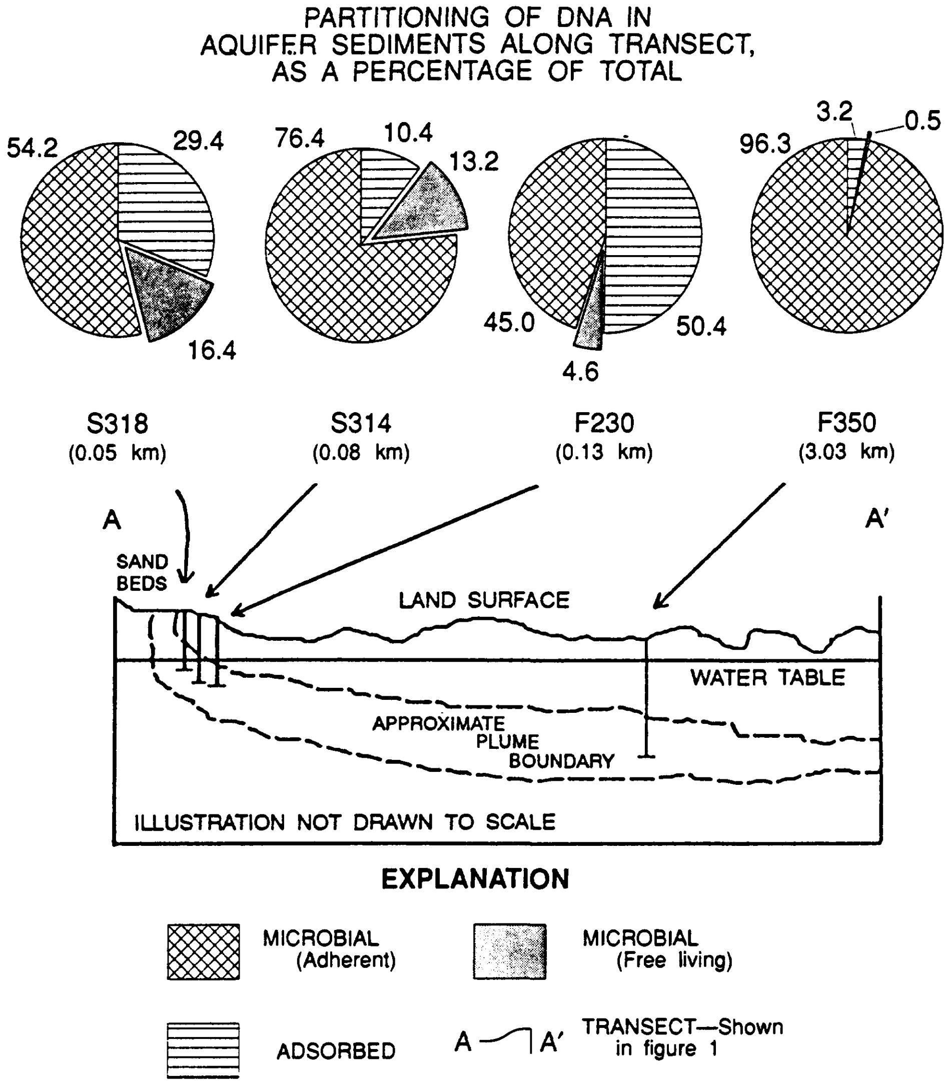

Figure 3. Illustration of total partitioning of DNA seen in aquifer sediments from Cape Cod Aquifer (km is kilometers).

contribute significantly to the overall DNA pool in freshwater sediments (Ogram and others, 1987; Steffan and others, 1988). The resistance of DNA to nuclease digestion in marine sediments (Lorenz and Wackernagel, 1987) may help to explain its persistence in sandy aquifer sediments.

In summary, despite the problems encountered with lysis of bacteria and recovery of DNA from sediments, the fluorometric DNA assay is a powerful tool for estimating biomass and determining biomass partitioning in contaminated aquifer sediments. However, the protocols used to determine DNA must account for partitioning between solid surfaces, adherent and free-living bacteria and eukaryotic microbes, sediment mineralogy, and differences in per-cell content of DNA.

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PRELIMINARY EVALUATION OF THE RELATIONS AMONG PROTOZOA, BACTERIA, AND CHEMICAL PROPERTIES IN SEWAGE-CONTAMINATED GROUND WATER ON CAPE COD, MASSACHUSETTS

By N.E. Kinner[1] , A.L. Bunn[1], Ronald W. Harvey[2], A. Warren[3] *and* L.D. Meeker[1]

ABSTRACT

Protozoa have a very important function in many surface water ecosystems, but have only recently been examined in aquifers. Preliminary studies indicated the presence of protozoa at the U.S. Geological Survey Cape Cod Toxic-Substances Hydrology Research site, located in Falmouth, Massachusetts. Because of the substantive background information on the hydrology, chemistry, and microbiology already collected at this site, a detailed study on the distribution, characterization, and ecological role of protozoa in the contaminant plume was started in 1990. The first phase of this research, which involved a plume-wide survey, revealed a large (more than 100,000 individuals per gram in some samples) and active protozoan population in parts of the contaminant plume. The protozoa were quite small (2-5 micrometers in diameter) and appeared to be present in oxic and anoxic parts of the plume. Some of the protozoa were encysted. The abundance and distribution of the protozoa indicate they are an important feature of the microbiological community and may directly or indirectly affect the fate of at least some organic contaminants in the plume.

INTRODUCTION

Protozoa are known to be effective predators on bacteria in marine, freshwater, soil, and wastewater environments. Data published during the 1980's by Sinclair and Ghiorse (1987; 1988) and by Hirsch and Rades-Rohkohl (1983) demonstrated that viable protozoa are present in ground water and subsurface environments. Based on their research, it was likely that protozoa would be present in the organic-compound-contaminated zones of the study site on Cape Cod, Mass. (fig. 1). This plume, which has resulted from the disposal of more than 1,700 cubic meters per day of treated sewage from the Otis Air Base onto rapid infiltration sandbeds, has been studied extensively as part of the U.S. Geological Survey Toxic Substances Hydrology Program. Some of the data collected at the Cape Cod site also indicated that protozoa might be present in the aquifer. For example, in closed-bottle incubation studies of the growth of the indigenous population of ground water bacteria from the site, prefiltration (3.0 μm (micrometer) pore size) and the presence of eucaryotic inhibitors (such as cyclohexamide) significantly increased net bacterial productivity (as determined by temporal changes in bacterial abundance) (R.W. Harvey, unpublished data on file in the Boulder, Colo. office of the U.S. Geological Survey).

In June 1987, we began preliminary investigations to determine if protozoa were present in the subsurface at the Cape Cod site by incubating slides in existing monitoring wells (the technique is described elsewhere in this paper). We subsequently designed and constructed several weighted stainless-steel downwell samplers to improve our recovery of protozoa. We also examined subsurface core material. Data collected from the downwell samplers and the cores indicated that protozoa were present in highly contaminated areas of the plume. In addition, various enumeration, isolation, and culturing techniques for protozoa were evaluated to choose the techniques best suited for use with the Cape Cod core material. On the basis of this preliminary research, we were encouraged to seek funding for a more extensive study of the distribution and role of the protozoa in the organically-contaminated subsurface. This research is currently being funded by the National Science Foundation (NSF).

The first phase of our NSF research project, a survey of protozoa, was conducted during October and November 1990. The purpose of the survey was to determine the spatial distribution of protozoa in a plume of organic-compound-contaminated ground water as a function of the physical and chemical conditions and the distribution of free-living and particle-bound bacteria. Vertical and horizontal transects along the plume were made. The horizontal transect consisted of 13 sites along the entire length of the plume, starting in the infiltration beds and concluding approximately 4 km (kilometers) downgradient. Vertical transects were made at three of the sites along the plume: one near the infiltration beds, one approximately 0.5 km downgradient, and one approximately 3 km downgradient in the part of the plume containing alkylbenzenesulfonate (ABS) detergents. In addition, core and ground-water samples were collected at a pristine control site. Two replicate cores were collected at each site and three subsamples of each core were analyzed. An evaluation of the intrasite variability in the core material from the Cape Cod subsurface showed that the largest source of variation in the data was associated with subsampling because of heterogeneity in grain size. The core material was analyzed for protozoa using a direct count epifluorescent-scanning technique and the Darbyshire most probable number (MPN) method. Particle-bound bacteria were enumerated by direct-count epifluorescence. Concurrently, downwell samplers were placed in wells adjacent to and at the same depths as the coring sites and left there for 4 weeks. Protozoa colonizing slides and the pore spaces in sponges attached to the samplers were enumerated immediately using differential-interference, light microscopy in the field. In addition, monitoring-well water was collected and analyzed for bacteria, dissolved organic carbon (DOC), specific conductance, pH, temperature, methylene-blue-active substances, dissolved oxygen, ammonia, nitrite,

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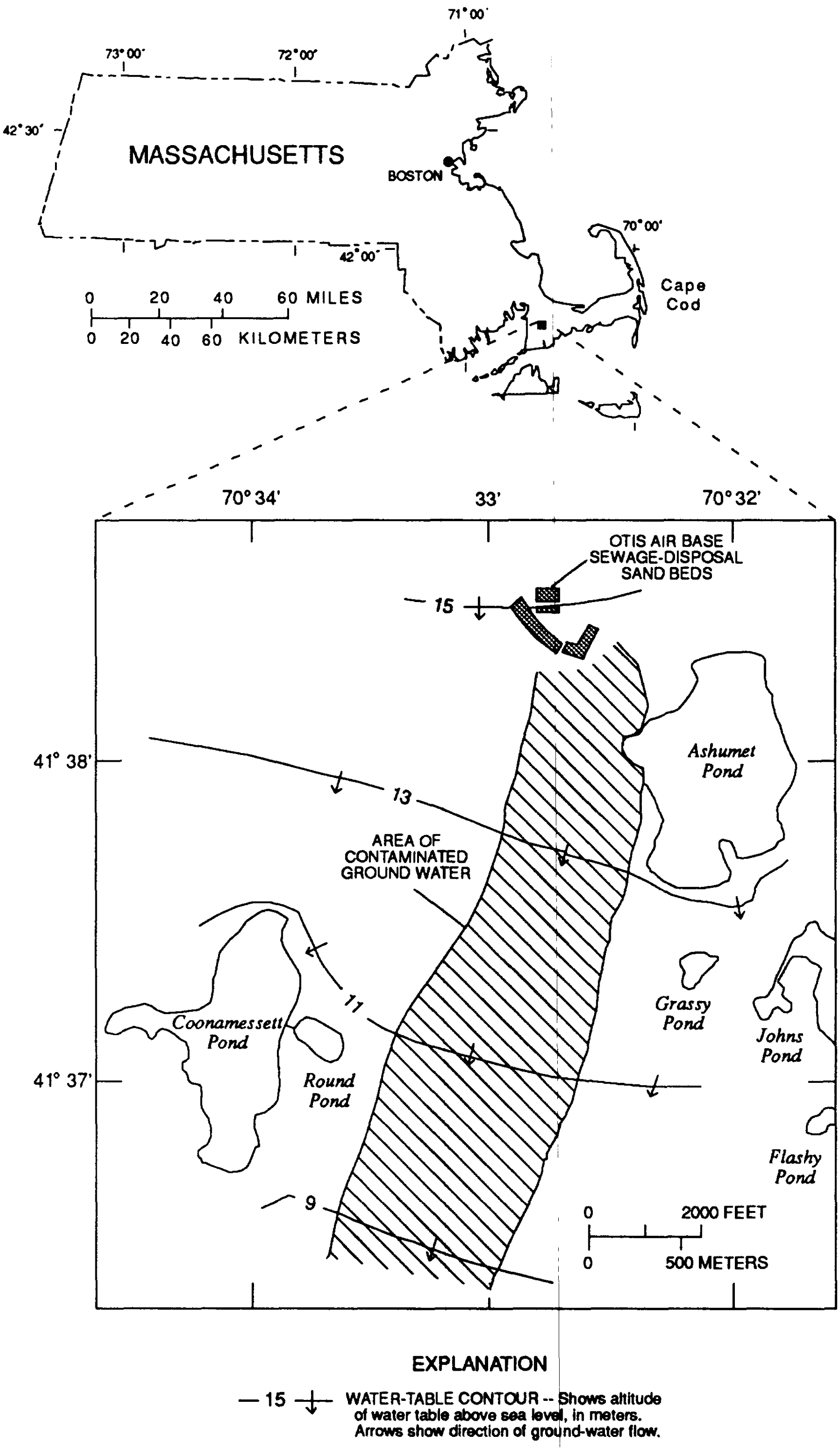

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OTIS AIR BASE SEWAGE-DISPOSAL SAND BEDS
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AREA OF CONTAMINATED GROUND WATER
Ashumet Pond
Coonamessett Pond
Round Pond
Grassy Pond
Johns Pond
Flashy Pond
0 2000 FEET
0 500 METERS
EXPLANATION
15 WATER-TABLE CONTOUR -- Shows altitude of water table above sea level, in meters. Arrows show direction of ground-water flow.

Figure 1. Location of study site on Cape Cod, Massachusetts.

nitrate, phosphate, and sulfate in order to determine the composition of the plume at each site.

The data will be analyzed statistically to determine possible correlations between the chemical composition of the plume, the degradation of organic contaminants (as evidenced by changes in the nonsurfactant DOC), and the abundance and distribution of bacteria and protozoa. In addition, statistical comparisons of the core and monitoring-well data will enable us to determine whether it is possible to construct an indicator scheme relating protozoan distribution in the contaminant plume to the protozoan abundance in the downwell samplers.

RESULTS AND DISCUSSION

Initial results, as of late November 1990, indicate that protozoan densities are as high as 10^5 organisms per gram dry weight in the core material recovered from the contaminated zones immediately downgradient from the source of contamination. These include primarily small flagellates (2-5 μm diameter) and some amoebae. In addition, the protozoa appear to inhabit both oxic and anoxic zones. Some of the protozoa appear to be encysted. The downwell samplers, especially the sponges, seem to give a good indication of the distribution of protozoa in the core material. Based on their numbers and diversity within the contaminant plume, protozoa appear to be significant constituents of the biological community in the subsurface, indicating that they may affect degradation of organic contaminants.

In summary, protozoa appear to be important constituents of the microbial communities in at least some contaminated aquifers. Although small in size, the large numbers of protozoa in parts of the contaminant plume at the Cape Cod Toxic-Substances Hydrology Research site suggest that these eucaryotes may have the potential to affect substantively the bacterial populations responsible for the biotransformations of the organic contaminants in the plume.

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SURVIVAL OF A MODEL POLLUTANT-DEGRADING MICROORGANISM IN A SAND AND GRAVEL AQUIFER AND IN MICROCOSMS

By M.L. Krumme[1], Richard L. Smith[2] *and* D.F. Dwyer[1]

ABSTRACT

In-situ bioremediation may involve the addition into contaminated environments of nonindigenous microorganisms that are capable of removing or degrading specific pollutants. Prior to their introduction into an environment, these microorganisms need to be assessed for their suitability as bioremediation agents and their potential to cause unwanted effects to that environment. We determined the usefulness of using microcosms to predict the in-situ fate of microorganisms added to aquifers by comparing the population dynamics of a model pollutant-degrading microorganism, Pseudomonas sp. B13 (B13) after introduction into laboratory microcosms and a sand and gravel aquifer. B13 was introduced into the aquifer in three depth intervals, where concentrations of dissolved oxygen were 10, 8, and 0 milligrams per liter and into microcosms, which contained aquifer core material from the same three depths. The B13 population was stable in all microcosms for 70 days after introduction. This was similar to results in the aquifer for two of the three depth intervals studied. In the depth interval where dissolved oxygen concentrations were 10 milligrams per liter, the population of B13 was not detected 70 days after introduction.

INTRODUCTION

There is a growing need to remediate contaminated aquifers because of an increasing shortage of high quality water supplies (Bitton and Gerba, 1984). *In-situ* bioremediation is one technique used for the elimination of contaminants and is proving to be environmentally acceptable and cost effective (Lee and Ward, 1985). This technique may involve the addition to contaminated environments of nonindigenous microorganisms that have been adapted to degrade or remove specific contaminants. The *in-situ* fate of these microorganisms needs to be assessed to determine whether the microorganism can survive and function within the environment and to evaluate the potential for the microorganism to affect the ecosystem adversely. We have developed aquifer microcosms that simulate a sand and gravel aquifer located on Cape Cod, Mass., and have used the microcosms to predict the *in-situ* fate of a model contaminant-degrading microorganism, *Pseudomonas sp.* B13 (B13). The purpose of this study was to determine the usefulness of these microcosms to predict the *in-situ* fate of microorganisms added to aquifers by comparing the population dynamics of B13 introduced into both microcosms and the sand and gravel aquifer. The aquifer has been contaminated with treated sewage, the degradation of which has caused an oxygen gradient within a contaminant plume. This situation allowed us to test survival of B13 under various concentrations of dissolved oxygen and contaminants. This paper presents the results of this study.

This work is the result of a collaboration between the German Institute of Biotechnology, Michigan State University, and the U.S. Geological Survey. It was supported, in part, through a Department of Energy grant (DE-FG02-89ER60848). This paper does not necessarily reflect the views of the Department of Energy and no official endorsement should be inferred.

METHODS AND RESULTS

Microcosms consisted of 15-mm (millimeters) X 200-mm acrylic columns filled with 40 grams of aquifer sediment to which B13 (10^6 microorganisms per gram of sediment) was added. Aquifer sediment was obtained from three different depths at one site, F347, in the aquifer (fig. 1). Depth-interval 1 (D1) was located 5.0 to 5.6 m (meters) below land surface (BLS), which was above the contaminant plume and contained 10 mg/L (milligrams per liter) dissolved oxygen; depth-interval 2 (D2) was located 5.9 to 6.6 m BLS within the contaminant plume and contained 8 mg/L dissolved oxygen; and depth-interval 3 (D3) was located 7.6 to 8.2 m BLS within the contaminant plume but contained only trace concentrations of oxygen (table 1). Ground-water samples from the three different depth intervals, D1, D2, and D3, were collected from multilevel sampling wells screened at depths of 5.6 m BLS, 6.7 m BLS, and 7.9 m BLS, respectively, in hospital infusion bags to minimize exposure of the ground water to oxygen. Ground water was pumped from the infusion bags through the microcosm columns at a rate similar to the flow rate of the aquifer (0.4 m per day). Microcosms were incubated in the dark at the *in-situ* temperature (12 °C (degrees Celsius)).

Table 1. *Sediment-sampling depth interval and ground water geochemistry for microcosm experiment*

Depth interval for microcosm sediments[1] (meters)	Depth of MLS[2] screen (meters)	Dissolved oxygen concentration (milligrams per liter)	Specific conductance[3] (microsiemens per centimeter)
5.0 - 5.6	5.6	10.4	43
5.9 - 6.6	6.7	8.1	82
7.6 - 8.2	7.3	0.1	158

[1] Samples collected at site F347, June-August 1990.
[2] MLS = Multilevel sampling device from which ground water was collected for microcosm experiments.
[3] At 25 degrees Celsius.

B13 was enumerated from the microcosms by sequentially sacrificing columns at 0, 7, 30, and 70 days, extracting the bacteria from the sediment and plating the extracts on media selective for B13. The number of B13 in microcosms remained constant for the 70-day study period (fig. 2).

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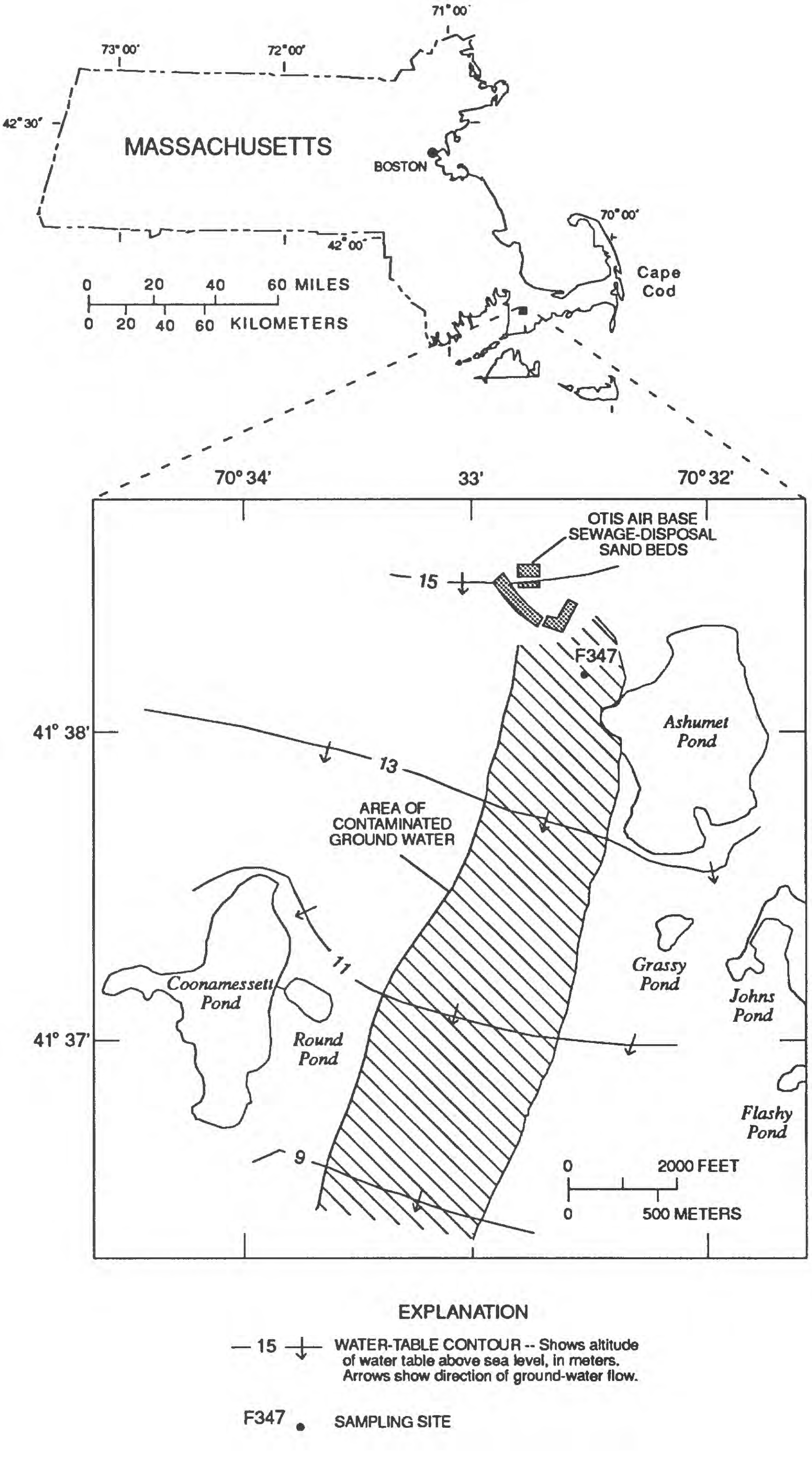
[2] U.S. Geological Survey, Boulder, Colo.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AREA OF CONTAMINATED GROUND WATER
Grassy Pond
Johns Pond
Coonamessett Pond
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Round Pond
41° 37'
Flashy Pond
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0 2000 FEET
0 500 METERS
EXPLANATION
15 WATER-TABLE CONTOUR -- Shows altitude of water table above sea level, in meters. Arrows show direction of ground-water flow.
F347 ● SAMPLING SITE

Figure 1. Ground-water study site on Cape Cod, Massachusetts, showing the location of the contaminant plume and the well site sampled for this study.

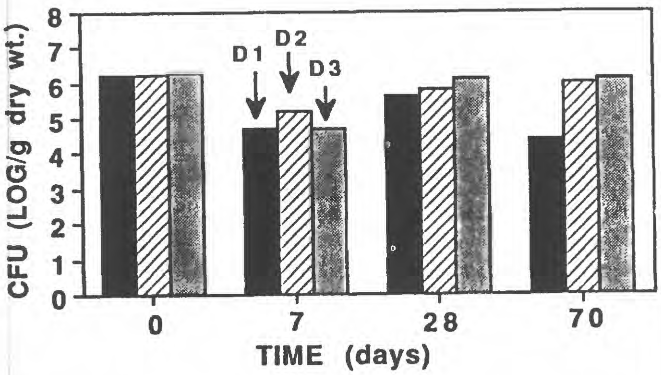

Figure 2. Enumeration of B13 as colony-forming units (CFU) in flow-through column microcosms. Microcosms contained sediment that originated from three different depth-intervals (D1, D2, D3) from the aquifer (see text).

Differences in the population dynamics of B13 were not observed between microcosms which contained aquifer sediments from the three different depths despite the differences in dissolved oxygen concentrations. On the basis of these microcosm studies, we predicted that the B13 population would remain stable for at least 70 days at each of the three depths, if B13 were introduced directly into the aquifer.

This prediction was tested by an *in-situ* survival experiment that involved injection of B13 directly into the aquifer at the three depths corresponding to those used in constructing the microcosms (fig. 3). Before injection, ground water (750 liters) was pumped from a nearby observation well into a waterbed mattress (a waterbed mattress was used to minimize exposure of the ground water to the atmosphere). Viable B13 and B13 stained with the fluorochrome 4',6-diamidino-2-phenylindole (DAPI) were added to the ground water at final densities of 10^6 and 10^7

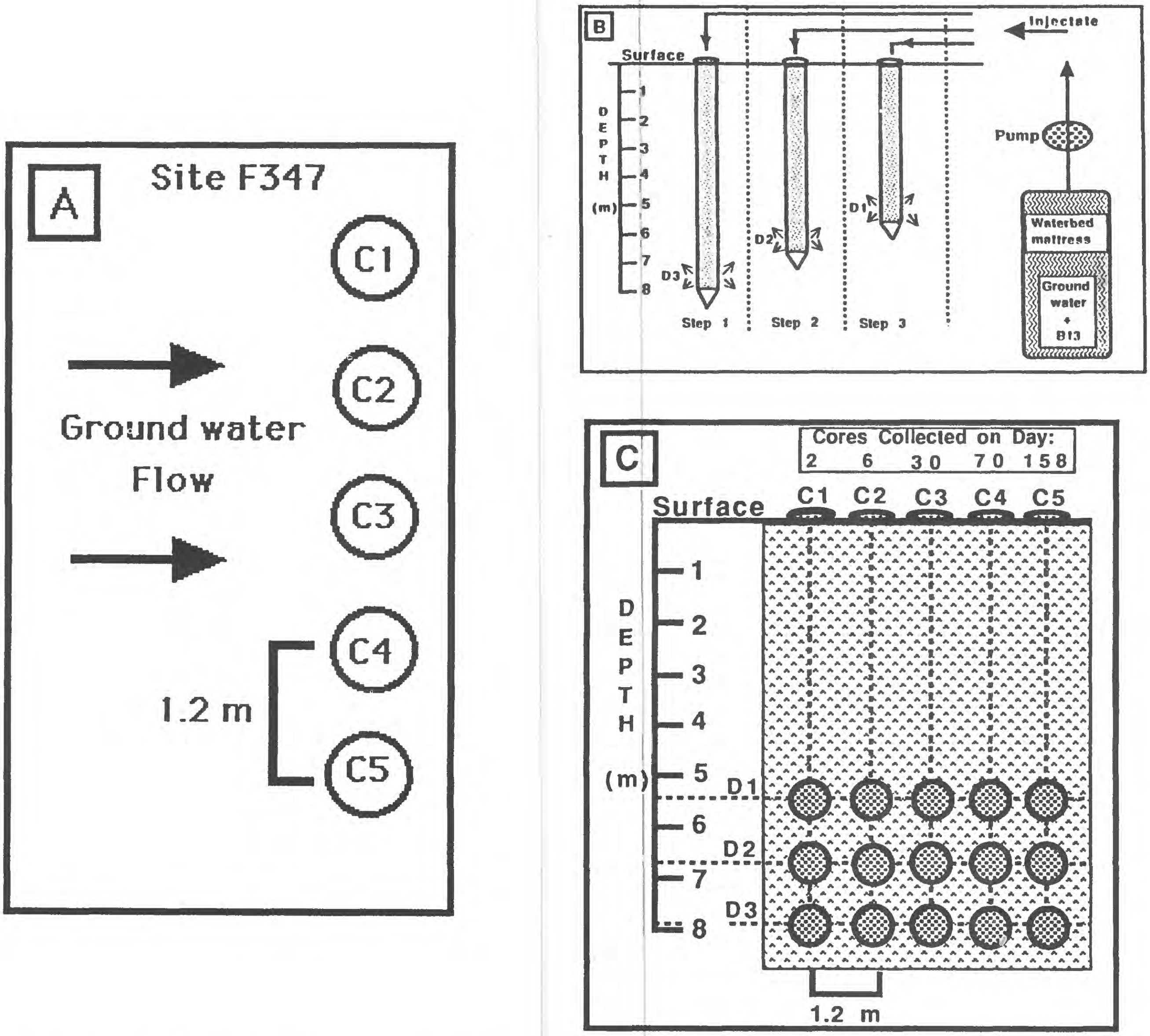

Figure 3. Procedure for the injection of B13 into the aquifer. (A) Plan view showing the arrangement of the five injection wells. Arrows show direction of ground-water flow. (B) Sequence for injection at the three different depth-intervals for one injection well. Ground water was obtained from a nearby well and pumped into a waterbed mattress. Viable B13 plus DAPI-stained B13 were added to the incoming flow of water. The bacterial suspension was simultaneously pumped into the aquifer through five removable well points (C1-C5) located at 7.9 m (Step 1). The procedure was repeated twice with the well points raised to 6.7 m (Step 2) and 5.5 m (Step 3), respectively. (C) The above procedure resulted in 15 tracer clouds (diameter = 0.9 m) containing B13 and DAPI-stained B13. The well points were removed after the injection was complete and sediment samples, one from each of the three depths at location C1, C2, C3, C4, and C5 were collected 2, 6, 30, 70, and 158 days, respectively, after injection of bacteria.

bacteria per milliliter, respectively. The resulting bacterial suspension was simultaneously pumped into the aquifer at site F347 through five removable well points (C1-C5) that were located in a row perpendicular to the flow of ground water (fig. 3A). The wells were constructed from steel pipe (1.9-cm (centimeter) outside diameter) and fitted with a slotted steel screen (length 5.1 cm). The screened end of all five well points had been placed at D3 (7.9 m BLS) and the injectate was simultaneously pumped into all five wells (fig. 3B). The entire procedure was repeated twice with the screened end of the well points raised first to 6.7 m BLS (D2) and then to 5.5 m BLS (D1). The well points were then removed and the holes in the aquifer allowed to collapse shut.

Changes in the number of bacteria over time were determined in sediment samples from one of the five injections sites (C1, C2, C3, C4, or C5) at 2, 6, 30, 70, and 158 days after injection, respectively (samples collected at 158 days are currently being analyzed). A splitspoon core barrel was used to collect sediment samples from each of the three injections depths, D1, D2, and D3 (fig. 3C). Because of the disturbance caused by the coring, each injection site was only sampled once, one injection site per time point. Sampling times corresponded to those used for the microcosms.

Viable B13 (non-DAPI stained) were enumerated by selective plating methods; DAPI-stained B13 were enumerated by means of epifluorescence microscopy (fig. 4). In addition to viability loss, the number of B13 in each sample could have been affected by transport of bacteria away from the injection (and sampling) site and(or) by any differences that may have occurred between injection sites during the injection and sampling procedures.

Thus, the DAPI-stained cells were used as a control to normalize the bacteria counts. If a steady number of DAPI-stained cells were observed, then it could be concluded that transport and injection or sampling problems had not occurred. Thus, subsequent changes in the number of viable B13 could be interpreted either as growth of B13 or removal of cells by predation or loss in viability.

B13 maintained a stable population for 70 days at two depths in the aquifer (D2 and D3) (fig. 4A). The number of B13 at D1 was stable for 30 days but, thereafter, decreased to undetectable levels. The number of DAPI-stained B13 remained constant in all three aquifer depths for the entire 70-day period (fig. 4B). Thus, the observed decrease in the numbers of viable B13 at D1 resulted from either a loss in viability or removal by predation.

SUMMARY AND CONCLUSIONS

On the basis of B13 counts when added to laboratory microcosms, we predicted that the survival of B13 would not be affected by the three different environments found within the contaminated aquifer. These predictions were correct for two out of the three depth-intervals (D2, D3) in the aquifer studied. The reasons for the decrease in the number of B13 in D1 in the aquifer, but not in the microcosms, are not known. Despite this difference, the laboratory microcosms were successfully used to predict the *in-situ* survival of B13 for 30 days in all three depth-intervals of the aquifer and for 70 days in the contaminated zones of the aquifer. The microcosms could not be used to make predictions beyond 30 days in the uncontaminated depth in the aquifer.

This type of microcosm can also be used to select microorganisms that survive in aquifers. For example, a comparison of the survival of B13 and its genetically modified derivative, *Pseudomonas sp.* B13 FR1 (pFRC20p), were made by enumerating both microorganisms when introduced into identical microcosms. In this way, it was possible to predict that the genetically modified derivative of B13 would also survive if it were released into the aquifer.

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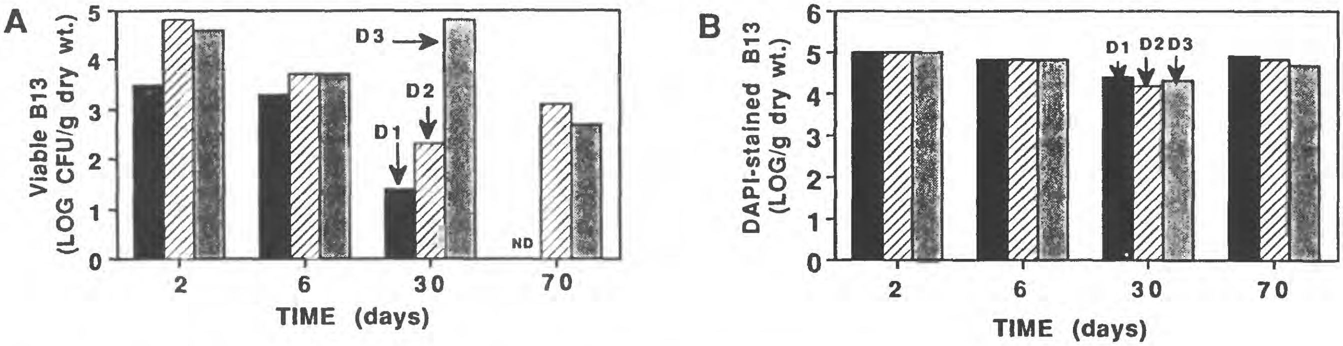

Figure 4. Enumeration of (A) viable B13 and (B) DAPI-stained B13 *in-situ* during aquifer injection experiment. B13 was injected into three different depth-intervals in the aquifer (D1, D2, D3) (see text). ND = not detected.

THE ROLE OF PHYSICAL AND CHEMICAL HETEROGENEITY IN THE INTERPRETATION OF SMALL-SCALE TRACER TESTS INVOLVING MICROORGANISMS

By Ronald W. Harvey[1], Stephen P. Garabedian[2], Richard L. Smith[1], Larry B. Barber, II[1],
David W. Metge[1], *and* Martha A. Scholl[3]

ABSTRACT

Transport of microorganisms in contaminated ground water is best studied in situ, because it is difficult to duplicate field conditions in the laboratory and the repacking of aquifer material into columns can significantly alter pore structure. A series of small-scale (6 to 12-meters travel distance), natural-gradient tracer experiments have been conducted at different locations and depths within an organically contaminated (treated sewage) section of an aquifer that had been instrumented with a 20- by 220 meter array of 15-port, multilevel samplers. The instrumented study area is part of the U.S. Geological Survey Cape Cod Toxic-Substances Hydrology Research site, located in Falmouth, Massachusetts. These tests have allowed assessment of differences in transport between various microorganisms, microspheres, and conservative tracers within different zones of the aquifer. Substantial differences in the relative transport between bacteria and microspheres and between bacterial-sized colloids and the conservative tracers were observed among sites. In some cases, these differences limited the transferability of models used to describe the downgradient bacterial migration. Therefore, interpretation can be complicated by physical and chemical heterogeneity, even though small-scale in-situ experiments provide more realistic information than do flow-through column studies. Comparisons of similar experiments performed at different locations and at different depths within the aquifer suggest that the effects of physical and chemical heterogeneity (grain-size distribution, preferred flow-path pore structure, ground-water chemistry, and mineralogy) upon observed transport of microorganisms and microbially-important substances need to be taken into account to describe the relative contributions of individual processes to bacterial transport.

INTRODUCTION

Because of their key role in contaminated ground-water environments, much attention is being focused on the measurement of bacterial movement and activity in contaminated aquifers. Models that simulate transport of bacteria and microbially mediated processes in ground water have employed conceptual and empirical approaches. For example, recent theoretical models involving microbial transport through porous media have incorporated a large number of governing processes (Corapcioglu and Haridas, 1984; 1985). However, verification of existing theoretical models by field observation is problematic, because of the complexity of the models and the number of parameters that need to be determined. Because the predictive value of these models can be limited (Germann and others, 1987), there is a need to develop more realistic models that are based on field observations.

As a result of laboratory and field transport investigations, important advances have been made toward improving an understanding of key processes governing microbial migration through aquifers. Columns packed with subsurface material allow experiments to be conducted with much greater control than is possible in field studies. Such experiments have allowed a clearer delineation of several factors governing microbial transport through the subsurface, including the effects of small porosity on size-dependent exclusion (Bales and others, 1989), survival (Bitton and others, 1979), sorption (Hendricks and others, 1979), and bacterial growth and taxis (Jenneman and others, 1985; Bosma and others, 1988; Reynolds and others, 1989). Column experiments have also proved useful in studying transport of genetically engineered bacteria before they are released into the subsurface (Trevors and others, 1990). However, it has also been shown that transport of microbes through subsurface sediments that have been repacked into columns can differ from that observed in the field, even when flow velocity, porosity, and physicochemical conditions are similar (Harvey, 1988). Therefore, the overall mathematical descriptions of bacterial transport through aquifers may necessitate more information derived from field investigations, inasmuch as repacking into columns can destroy the original secondary (preferred flow path) pore structure or fabric (Smith and others, 1985).

There have been few reported attempts to model *in-situ* observations of bacterial transport through part of an aquifer. One such model was used to simulate breakthrough curves for fluorochrome-labeled indigenous bacteria (whole population) that had been injected into sandy (0.59-millimeter median grain size) aquifer sediments 7 m (meters) upgradient (Harvey and Garabedian, 1991). Coinjection of a conservative tracer with the labeled bacteria facilitated construction of the hydrologic part of the model. A solute-transport model also has been employed in the simulation of microbial transport through saturated sediment in column experiments with nonsorbing viruses (Grondin and Gerba, 1986). The model described by Harvey and Garabedian (1991) includes terms for storage, advection, dispersion, and reversible, and irreversible sorption. The deterministic approach employed was satisfactory because the horizontal extent of the layers having similar conductive properties, as delineated by hydraulic conductivity profiles, appeared to be on the order of several meters (Hess, 1989) and, at that particular site, there appeared to be little physical heterogeneity, as evidenced by the idealized nature of the tracer and bacterial breakthrough curves.

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However, the magnitude of immobilization, retardation, and differential size exclusion of the bacteria from small porosity can differ significantly over small distances (several meters) within this aquifer. This paper describes apparent differences in relative transport between bacteria, bacteria-sized microspheres, and conservative tracers among *in-situ* transport experiments involving different zones within a stratified, sandy aquifer.

RESULTS AND DISCUSSION

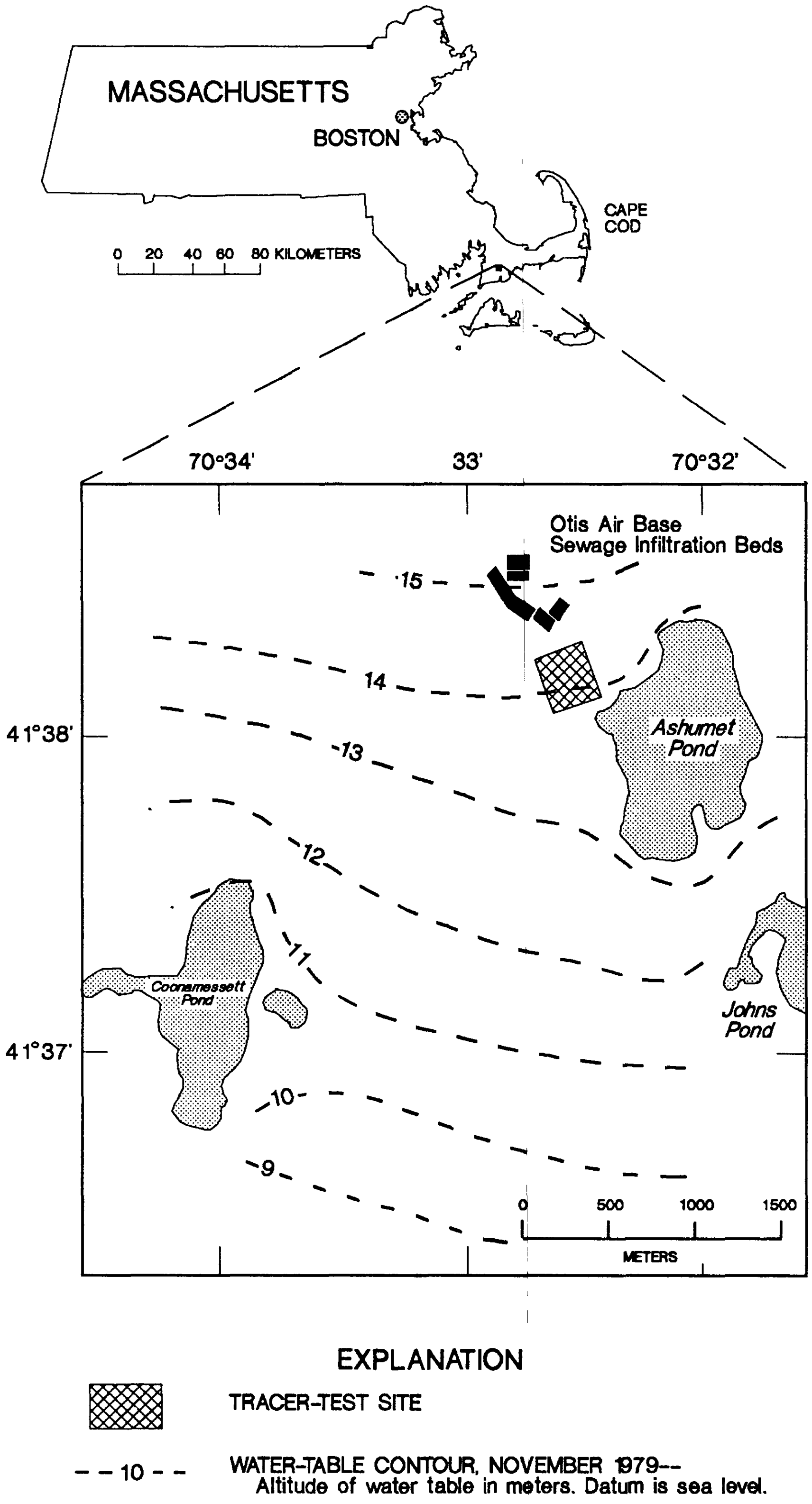
The effect of aquifer heterogeneity on the transport of bacteria and microspheres relative to a conservative tracer (bromide) was most evident in a tracer test performed during May and June 1990. The experiment involved collection of 97 liters of ground water collected at 8.8 and 9.0 m BLS (below land surface) from multilevel sampling device (MLS) 7-15 and slow reinjection into the aquifer along with bromide (154 milligrams per liter), indigenous ground water bacteria (4.30 ± 1.66 × 10^9/L) that had been previously labeled with the fluorescent dye DAPI 4',6-diamidino-2-phenyl-indole, and carboxylated microspheres (1.16 ± 0.12 × 10^9/L). Bromide, stained-bacteria, and microspheres were monitored as they moved with the natural flow of ground water past rows of MLS, spaced 2 m apart in the large MLS array identified in figure 1. The tracer cloud was monitored for a distance of 12 m. At 6 m downgradient, the tracer cloud appeared to strike MLS 10-14 directly, allowing accurate delineation of the concentration histories of the bromide, bacteria, and microspheres at three different depths within the aquifer. At 8.8 m BLS, the bacterial breakthrough curve was bimodal, exhibiting a peak that clearly preceded the single observed bromide peak and a second peak that clearly lagged behind the bromide peak. The microsphere breakthrough exhibited a single peak that was coincident with the retarded (later) peak in bacterial abundance. At 9.0 m BLS, the bromide and bacterial breakthrough patterns were quite similar, both exhibiting coincident, single peaks. However, the microspheres were clearly retarded with respect to both bacteria and bromide. Finally, at 9.5 m BLS, the breakthrough curves for all three constituents were similar--that is, all exhibited single peaks that were coincident and similar in shape.

In a number of experiments performed at the Cape Cod site, breakthrough curves of the labeled microorganisms that were injected into the aquifer upgradient matched those of the conservative tracer rather closely (Harvey and others, 1989; Harvey and Garabedian, 1991). However, this is usually not the case in aquifers in fractured crystalline rock (Champ and Shroeter, 1988). Earlier peak breakthrough of microorganisms is often observed in small-scale injection tests involving fracture flow where there is a good deal of secondary pore structure. The earlier arrival of DAPI-stained bacteria relative to bromide in at least one earlier test performed at the Cape Cod site (for example, Harvey and others, 1989) suggests that some secondary pore structure may exist, at least in places, within the relatively well-sorted sediments of this aquifer. Later arrival of at least part of an injected bacterial population relative to a conservative tracer is often but not always observed. Hence, retardation can also differ within the aquifer.

A number of aquifer properties may affect the degree of immobilization and(or) retardation including the grain size distribution, flow velocity, ground-water temperature and chemistry, and mineralogy. Changes in hydraulic properties and ground-water chemistry may occur over a relatively short distance, particularly along vertical transects through the contaminant plume. The ionic strength in the core of the plume is about tenfold higher than in adjacent, uncontaminated ground water, because of the relatively high concentrations of total dissolved solids (DS). The high pH of the treated-sewage effluent and *in-situ* production of bicarbonate alkalinity by ground-water microbes reduces the pH in the core of the plume (6.0-6.5) compared to the pH of the moderately acidic ground water in the zone of recharge above and below the plume (4.5-5.0). Also, although uncontaminated ground water in the region appears to be near saturation with respect to dissolved oxygen (DO), much of the core of the plume is DO-depleted as a result of aerobic degradation of the dissolved organic contaminants by the ground-water microbial populations. Temperature in the core of the plume ranges up to 8 °C (degrees Celsius) higher than uncontaminated ground water near the water table. The resulting gradients in DO, pH, DS, temperature, and dissolved organic carbon along vertical transects through the plume allow for assessment of bacterial transport under different conditions.

Chemical changes within the contaminant plume can lead to differences in reversible sorption, which controls retardation, and irreversible attachment, which controls attenuation. The degree of "tailing" in microbial breakthrough curve relative to that observed for the conservative tracer is indicative of reversible sorption behavior and varies from site to site. In one tracer test conducted at the ambient pH value of 5.8 at MLS 7-15, partial desorption of the stained-bacteria that had previously sorbed onto aquifer sediment particles immediately downgradient from the injection well was affected by injecting ground water with the pH adjusted to 7.8. In another experiment, little retardation was observed (Harvey and others, 1989). Physical heterogeneity can also lead to changes in the relative contributions of straining and sorption in immobilization of microorganisms, possibly because of changes in the size distribution of intergranular pores and in the properties of grain surfaces.

In summary, it appears likely that physical and chemical heterogeneity within a contaminated, sandy aquifer can have a very significant effect on the apparent transport of bacteria and bacteria-sized colloids moving through those sediments. This heterogeneity can have a key effect on the factors, such as attenuation, apparent (hydrodynamic plus chemical plus sorptive-induced) dispersion, and retardation, that determine the observed differences between the bacteria, microsphere, and conservative tracer breakthrough curves. It is clear that modeling efforts to describe microbial transport in sandy sediments may benefit from additional information on the role of physical and chemical variability on the controls of microbial transport.


MASSACHUSETTS
BOSTON
CAPE COD
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10
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Ashumet Pond
Coonamessett Pond
Johns Pond
0 500 1000 1500
METERS
EXPLANATION
TRACER-TEST SITE
WATER-TABLE CONTOUR, NOVEMBER 1979--
Altitude of water table in meters. Datum is sea level.

Figure 1. Ground-water study site on Cape Cod, Massachusetts, showing the location of the contaminant plume and the well site sampled for this study.

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LABORATORY STUDIES OF BACTERIAL SORPTION TO AQUIFER SEDIMENTS FROM THE CAPE COD TOXIC-SUBSTANCES HYDROLOGY RESEARCH SITE

By Martha A. Scholl[1] *and* Ronald W. Harvey[2]

ABSTRACT

Field tests in the aquifer at the Cape Cod Toxic-Substances Hydrology Research site have shown that bacterial sorption to sediment surfaces is an important process affecting bacterial transport. A nonstirred batch method was used to study bacterial sorption in the laboratory under simulated aquifer conditions, using contaminated and uncontaminated ground water collected at the site. The pH-dependency of bacterial sorption and the degree of bacterial sorption to different surface types (untreated, organic matter removed, organic matter and oxyhydroxides removed) was determined in both types of ground water. Desorption of bacteria in the presence of phosphate buffer at pH 8 was shown to occur. The experiments indicate that geochemical conditions can affect bacterial mobility in the aquifer.

INTRODUCTION

Bacterial transport in contaminated ground water is a subject of current interest, because bioremediation is a possible solution to some contamination problems. Bacterial-transport experiments at the Cape Cod site (Harvey and others, 1989) have shown that sorption of bacteria to aquifer sediments is an important determinant of the extent of transport along a flow path. Laboratory experiments were undertaken to study the bacterial sorption process in more detail. The objectives of the study were to (1) develop a nonstirred batch method to study bacterial sorption, (2) determine how the amount of sorption varies under different geochemical conditions, and (3) determine whether changes in geochemical conditions result in desorption of bacteria. The results presented here show the effects of variations in pH and sediment-surface coating on bacterial sorption in contaminated and uncontaminated ground water, and desorption of bacteria in the presence of a phosphate buffer.

METHODS

The method developed was a simple flow-through system that used aquifer sediments, ground water, and bacteria from the field site. The columns were glass, 20-cubic-centimeter syringes packed with 10 grams of sieved (0.5- to 1.0-millimeter size fraction) core material from contaminated or uncontaminated locations at the field site. Bacteria were concentrated by filtration from a water sample collected from directly below the sewage infiltration beds, stained with DAPI (a DNA-specific fluorochrome), rinsed, and added to the top of each column. The experiments were run at 10 °C (degrees Celsius) for 5 hours; preliminary studies indicated that sorption of bacteria was virtually complete within 5 hours. After the 5-hour attachment period, the sand was rinsed with 15 or 20 milliliters of ground water, and the eluted bacteria were counted by epifluorescent microscopy. The fraction of cells retained in the columns was then determined by difference. Experiments were performed with contaminated (ionic strength (I) = 4.0×10^{-3}, dissolved organic carbon (DOC) approximately 4 mg/L (milligrams per liter)) or relatively uncontaminated (I = 8.8×10^{-4}, DOC approximately 0.4 mg/L) ground water collected at the site.

RESULTS AND DISCUSSION

Sorption experiments were performed using aquifer sediments from an uncontaminated area of the aquifer equilibrated with contaminated or uncontaminated water at pH of 3 to 9. The pH- dependency of bacterial sorption onto aquifer sediments varied depending on whether sorption occurred in contaminated or uncontaminated water (fig. 1). In uncontaminated water, numbers of attached cells varied from 56 to 77 percent of the bacteria added to the columns. Sorption increased with decreasing pH, consistent with the sorption behavior of dissolved organic species to oxide surfaces (Davis, 1982). In contaminated water, bacterial sorption was less responsive to differences in pH. The number of cells sorbed did not vary more than 12 percent with changes in pH, suggesting that a different attachment process occurred in the contaminated water. Perhaps bacterial sorption was affected by a surface layer of organic material adsorbed from the contaminated water. Another possibility is that bacterial sorption was affected by divalent ions in solution.

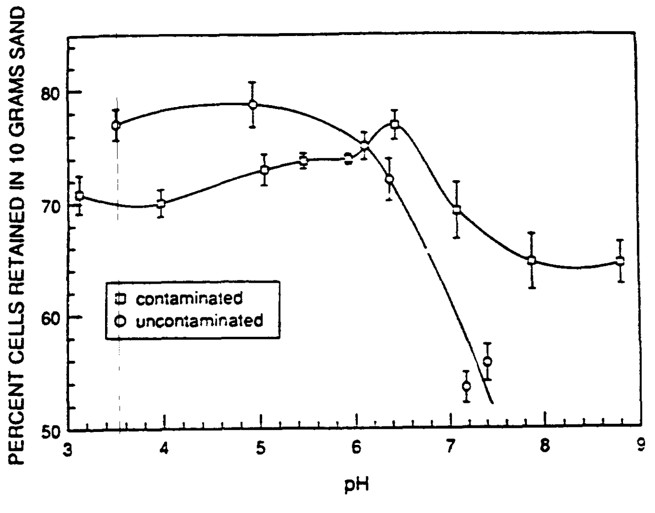

Figure 1. Effect of pH on bacterial sorption to Cape Cod aquifer material in contaminated and uncontaminated ground water. Error bars are one standard error.

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[2] U.S. Geological Survey, Boulder, Colo.

Sorption to different types of sediment surfaces that bacteria might encounter in the aquifer at the field site was tested using core material from a contaminated area of the aquifer. The core material was treated with 0.1 M (molar) NaOH for 3 hours to remove organic surface coatings, or sequentially with 3 percent oxalic acid at 70 °C for 1 hour to remove iron oxy hydroxide coatings (Chao and Zhou, 1983). Untreated sediment was used as a control. Bacterial attachment to oxalate- and NaOH-treated sediments was greater in contaminated ground water than in uncontaminated ground water. The pattern of sorption to the treated sands was also different in the two ground waters (table 1).

Table 1. *Percentage of injected bacteria sorbed to untreated, NaOH-treated and oxalate-treated sand from the Cape Cod aquifer*

[Values are the mean of four replicates plus or minus one standard error]

	Contaminated water	Uncontaminated water
Untreated sand	42.4± 1.6	43.5± 2.8
NaOH-treated sand	49.8± 2.2	40.0± 3.5
Oxalate-treated sand	48.1± 2.6	26.7± 4.5

In uncontaminated water, the degree of attachment of bacteria to untreated and NaOH-treated sand, both of which had iron oxyhydroxide coatings, was similar. The degree of attachment to oxalate-treated sand was significantly lower. In contaminated water, the degree of bacterial sorption to the untreated sand was the lowest, and the amount of sorption to NaOH- and oxalate- treated sand was effectively the same. This suggests that positive surface charge associated with oxyhydroxide coatings on grain surfaces was masked by DOC adsorbed from the water or present as coatings on the sand grains, as is seen in other natural systems (Davis, 1982). The above experiments are being investigated further by using artificial ground water with minimal levels of DOC and varying the concentrations of divalent ions.

Desorption studies were undertaken to determine the number of bacteria that were "reversibly" sorbed--that is, released from the columns because of a change in chemistry of the pore fluid. Phosphate buffer (0.05 M) at pH 8 was used to desorb attached cells after unattached cells were rinsed through the columns. Phosphate-rinsed columns were compared to columns rinsed with additional ground water. The results indicated that few cells (about 2 percent of the total injection) were desorbed by the treatment.

In summary, bacterial attachment to grain surfaces in the aquifer appears to be affected by ground water and sediment chemistry. Field (unpublished data on file in the Menlo Park, Calif., office of the U.S.Geological Survey) and laboratory evidence both suggest that bacteria can be desorbed by changes in solution chemistry. However, the time dependence of the desorption process is uncertain, because some bacteria are known to produce exopolymer with which they firmly attach themselves to surfaces. The experiments indicate that geochemical conditions in aquifers can significantly affect the mobility of bacteria traveling through porous media.

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RESEARCH IN FRACTURED-ROCK HYDROGEOLOGY: CHARACTERIZING FLUID MOVEMENT AND CHEMICAL TRANSPORT IN FRACTURED ROCK AT THE MIRROR LAKE DRAINAGE BASIN, NEW HAMPSHIRE

By Allen M. Shapiro[1] *and* Paul A. Hsieh[2]

ABSTRACT

Many scenarios of anthropogenic waste isolation consider burial in unconsolidated near-surface deposits; these wastes, however, can leach into the underlying bedrock. Fractures in the bedrock have the capacity to transport contaminants rapidly over large distances, and therefore, can have a great effect on ground-water and surface-water resources. Prediction of fluid movement and chemical transport in fractured rock is a complex task because of the difficulty in physically identifying and mathematically characterizing the spatial variability of hydraulic properties of the bedrock over various length dimensions. This problem is encountered in all subsurface flow regimes, but it is most acute in fractured rock because of the extreme spatial variability and the abrupt spatial changes in hydraulic properties. These conditions make it difficult to design field experiments and to employ interpretive methods of predicting fluid movement and chemical transport that were developed for application to unconsolidated porous media.

A multidisciplined research project is being conducted in the bedrock of the Mirror Lake drainage basin in the Hubbard Brook Experimental Forest in central New Hampshire to address these problems in fractured-rock hydrogeology. The principal objectives of this study are to: (1) develop methods of monitoring hydraulic and chemical data in heterogeneous bedrock flow regimes; (2) develop hydraulic, tracer, geophysical and geochemical field techniques and interpretive methods to identify hydraulic and transport properties of bedrock and to characterize fluid movement and chemical transport over various length dimensions; (3) improve upon interpretive models of fluid movement and chemical transport in bedrock by incorporating geologic, lithologic, and fracture mapping data; and (4) establish a site for long-term monitoring of bedrock environments and a controlled field-scale laboratory to test new equipment and interpretive analyses for characterizing and predicting fluid movement and chemical transport in fractured rock.

INTRODUCTION

Investigations that specifically consider fluid movement and chemical transport in fractured rock are relatively recent in relation to the overall history of quantitative hydrogeology. Many of the first investigations of fluid movement in fractured rock were conducted by petroleum geologists to assess the recovery of petroleum resources. In hydrogeology, however, interest in fractured rock and the need to adopt conceptual models different from those applied in unconsolidated porous media have stemmed from a gradual shift in emphasis over the past 30 years from investigations of water quantity to analyses of subsurface-water quality. Many of the initial hydrogeologic investigations associated with fractured rock were prompted by the need to assess geologic settings for the burial of anthropogenic wastes--in particular, sites for high-level, radioactive-waste isolation. Recently, however, investigations of fractured rock have become more widespread. The leaching of hazardous and toxic substances from unconsolidated near-surface porous media to fractured bedrock poses a threat to the water resources of many communities. The fractures represent avenues of high permeability within an otherwise low-permeability matrix. Thus, fractures have the capacity to transport fluid and contaminants rapidly over large distances.

Over the short history of quantitative fractured-rock hydrogeology, the difficulty in developing interpretive methods and field techniques to characterize fluid movement and chemical transport is widely recognized in all but the simplest of geologic settings. One of the principal problems that is faced in quantitative fractured-rock hydrogeology is identifying and mathematically characterizing the spatial heterogeneity of hydraulic properties of the bedrock over various length dimensions. The spatial variability of hydraulic properties controls fluid movement, which, in turn, is the principal component affecting chemical transport. The problem of characterizing spatially variable hydraulic properties over various length dimensions is not synonymous with fractured rock; it is also a problem in unconsolidated porous media. However, the problem is most acute in fractured rock because hydraulic properties can vary over more than 8 orders of magnitude, and are subject to abrupt spatial changes. In contrast, unconsolidated porous media are characterized by smaller ranges of hydraulic properties that usually are not subject to abrupt spatial changes. The abrupt spatial changes in hydraulic properties of the bedrock arise because thin highly permeable fractures are complexly interconnected within a rock matrix of low permeability. Consequently, the majority of fluid and chemical constituents in bedrock can be conducted through a small volume of the rock, making it difficult to design field experiments and employ interpretive analyses of fluid movement and chemical transport designed for unconsolidated porous media. Even if the bedrock is highly fractured, the formation is not necessarily analogous to an unconsolidated porous medium, because not all fractures are capable of conducting fluid.

In the relatively short history of fractured-rock hydrogeology, much has been done with regard to theoretical interpretations of fluid movement and chemical transport, but far less has been accomplished with regard to detailed field investigations that appraise the theoretical approaches.

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[1] U.S. Geological Survey, Reston, Va.
[2] U.S. Geological Survey, Menlo Park, Calif.

Field investigations in fractured rock are costly because of the expense associated with drilling and testing. Thus, field investigations that have not been directed toward high-level, radioactive-waste isolation are conducted using a limited number of boreholes and with limited use of investigative hydrogeologic approaches, such as collaborative efforts between hydraulic, geophysical, and geochemical field techniques and interpretive methods. Although limitations on the number of boreholes will always be a problem, a single investigative approach will not provide an adequate means of predicting fluid movement and chemical transport because of the complexity of most fractured-rock flow regimes. If progress is to be made in the development of interpretive methods and field techniques to characterize fluid movement and chemical transport in fractured rock, it must be accomplished through a collaborative research effort based on extensive field investigations that correlate information and interpretive methods of hydraulic, geochemical, and geophysical techniques along with geology, lithology, and fracture mapping.

A multidisciplinary research project in fractured-rock hydrogeology is being conducted in the Mirror Lake drainage basin at the Hubbard Brook Experimental Forest in central New Hampshire (fig. 1) to address questions in characterizing fluid movement and chemical transport in fractured rock. This research project is supported by the U.S. Geological Survey (USGS) Toxic Substances Hydrology Program and the National Research Program (NRP) in the Water Resources Division (WRD), and is being conducted by USGS personnel in the NRP, the New Hampshire and Connecticut State Offices in the New England District, and in the Geologic Division, as well as personnel from outside research institutes. The principal objectives of the study are to: (1) develop methods of monitoring hydraulic and chemical data in heterogeneous bedrock flow regimes; (2) develop hydraulic, tracer, geophysical and geochemical field techniques, and interpretive methods to identify hydraulic and transport properties of bedrock for characterizing fluid movement and chemical transport over various length dimensions; (3) improve upon interpretive models of fluid movement and chemical transport in bedrock by incorporating geologic, lithologic, and fracture mapping data; and (4) establish a site for long-term monitoring of bedrock environments and a controlled field-scale laboratory to test new equipment and interpretive analyses for characterizing and predicting fluid movement and chemical transport in fracture rock. This paper provides a brief overview of the hydrogeology of the Mirror Lake drainage basin and the scope of the field investigations that are to be conducted.

SITE DESCRIPTION AND PREVIOUS INVESTIGATIONS

The Mirror Lake drainage basin is adjacent to the Hubbard Brook Experimental Forest in the White Mountains of central New Hampshire (fig. 1). The Hubbard Brook Experimental Forest and most of the Mirror Lake drainage basin are managed by the U.S. Department of Agriculture Forest Service. This area is the site of numerous long-term hydrologic and biogeochemical investigations related to watershed management. The Mirror Lake drainage basin, located at the mouth of the Hubbard Brook Valley, is a small, well-defined hydrologic environment covering approximately 85 ha (hectares) (Winter, 1985). Mirror Lake covers an area of approximately 15 ha and is at an elevation of 213 m (meters) above sea level (Winter, 1985). The highest elevations in the watershed (approximately 469 m) are to the north and west of Mirror Lake. Outflow from Mirror Lake enters Hubbard Brook, which is a tributary of the Pemigewasset River.

The bedrock in the Mirror Lake drainage basin is primarily schist of a sillimanite grade that has been extensively intruded by granite. Lesser amounts of pegmatite and basalt also have intruded into the granite and schist. Successive orogenies have caused folding and faulting that have resulted in extensive fracturing in the bedrock. Roadcuts exposed along Interstate 93, east of the Mirror Lake drainage basin, show highly irregular configurations and dimensions of the granite, schist, pegmatite and basalt.

The bedrock surface in the Mirror Lake drainage basin is characterized by a saddle that underlies the south-central part of Mirror Lake (Winter, 1985). The bedrock surface rises to the east and to the west, and bedrock valleys descend to the north and south of the saddle. Unconsolidated glacial deposits (drift) overlie the bedrock. To the west and northwest of Mirror Lake, the glacial deposits are predominantly till, approximately 10 m thick. Thicknesses of till of up to 50 m have been encountered north of Mirror Lake, corresponding to the location of the bedrock valley. To the south of Mirror Lake are deposits of till, but extensive areas of sand and gravel are also present, especially in the vicinity of the lake outlet (Winter, 1985). The configuration of the bedrock surface indicates that Mirror Lake is situated in, and is underlain by, glacial deposits. In addition, a thick layer of dense sediments lies at the bottom of Mirror Lake (Winter, 1985). The average depth of Mirror Lake is approximately 6 m, and its maximum depth is 11 m (Winter, 1985).

Mirror Lake is the subject of numerous biological and chemical investigations of the lake ecosystem. A summary of many of these investigations, which began in the early 1960's, is reported in a book edited by Likens (1985). Extensive investigations of the hydrology of Mirror Lake and the Mirror Lake drainage basin are also being conducted. Winter (1984; 1985) described the hydrogeologic setting of Mirror Lake and the instrumentation used to monitor all components of the hydrologic system in the Mirror Lake drainage basin. Flows of all streams leading to Mirror Lake are measured with recorders and flumes; precipitation is measured at two locations in the drainage basin; and climatological information for energy budget and evaporation studies have been collected since 1983. In addition, hydraulic heads are monitored in piezometers and water table wells in the drift and bedrock wells that are areally distributed in the Mirror Lake drainage basin. Hydraulic heads indicate that the bedrock is a dynamic part of the ground-water flow regime (Winter, 1984).

A preliminary survey of the ground-water chemistry in the drift and the bedrock was conducted by collecting water samples from piezometers and water-table wells in the drift and bedrock wells (J.W. LaBaugh, U.S. Geological Survey, written commun., 1988). This survey was compiled from

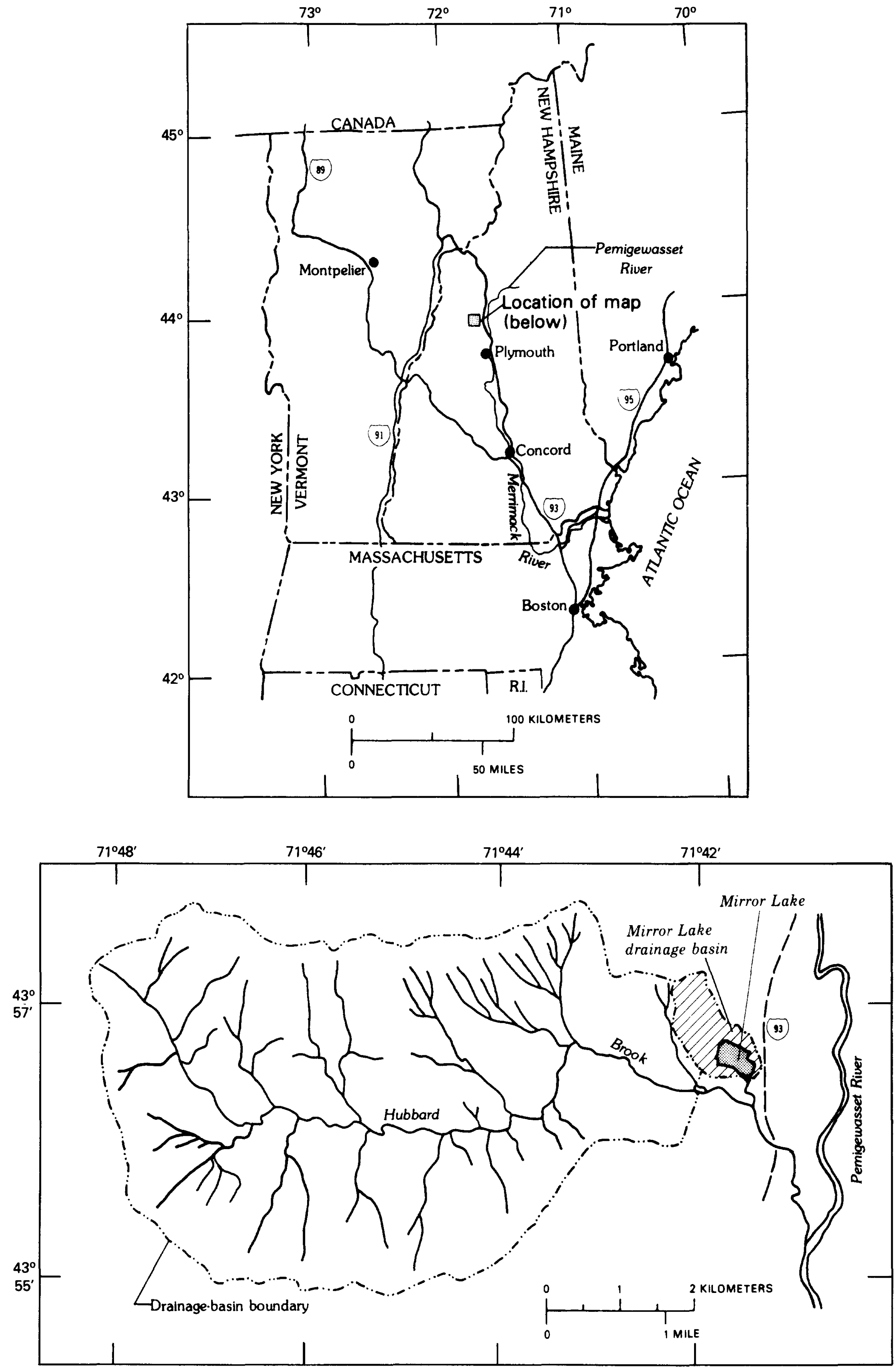
73°
72°
71°
70°
45°
44°
43°
42°
CANADA
MAINE
NEW HAMPSHIRE
89
Montpelier
Pemigewasset River
Location of map (below)
Plymouth
Portland
95
91
NEW YORK
VERMONT
Concord
Merrimack River
93
ATLANTIC OCEAN
MASSACHUSETTS
Boston
CONNECTICUT
R.I.
0
100 KILOMETERS
0
50 MILES
71°48′
71°46′
71°44′
71°42′
43° 57′
43° 55′
Mirror Lake
Mirror Lake drainage basin
93
Brook
Hubbard
Pemigewasset River
Drainage-basin boundary
0
1
2 KILOMETERS
0
1 MILE

Figure 1. Location of Hubbard Brook Experimental Forest and Mirror Lake drainage basin in New Hampshire (from Winter, 1985).

samples collected during 1983-87. The results of this survey indicate that the ground water in the Mirror Lake drainage basin is a calcium bicarbonate type. From this preliminary survey, spatial variation in chemical characteristics of the ground water could not be related to topographic location in the drainage basin. In addition, the frequency of sampling did not make it possible to identify temporal variability in the chemical characteristics of the ground water in the drift or bedrock.

Investigations identifying fracturing and hydraulic properties were conducted in many of the bedrock wells in the Mirror Lake drainage basin. Borehole geophysical logs were used to identify lithology, fractures, fracture orientation, and mineral alteration in fractures (Paillet, 1985; Paillet and Kapucu, 1989). A high resolution, heat-pulse flowmeter identified natural flow in boreholes, water-producing fractures, and the interconnection between adjacent boreholes (Paillet, Hess, Cheng, and Hardin, 1987). Vertical seismic-profile measurements and the analysis of acoustic waveforms were used to estimate hydraulic properties of fractures (Hardin and others, 1987; Paillet, Cheng, and Hsieh, 1987). Hydraulic properties of fractures were also estimated by use of single-hole injection tests conducted by isolating discrete intervals of the borehole with inflatable packers (Hsieh, 1987). Hsieh (1987) also conducted cross-hole hydraulic tests to characterize the rock mass between adjacent boreholes. The results of these geophysical and hydraulic investigations indicated that the bedrock is highly fractured, but that only a small part of the fractures have significant permeability. Furthermore, the bedrock is highly heterogeneous and the permeable fractures are sufficiently sparse over the dimensions of the crosshole tests (approximately 9.1 m separating adjacent boreholes); as a result, the rock mass does not hydraulically respond as a uniform porous continuum (Hsieh, 1987).

SCOPE OF FIELD INVESTIGATIONS

The principal problem facing the field characterization and prediction of fluid movement and chemical transport in fractured rock is the physical identification and mathematical characterization of the spatial variability in hydraulic properties of the bedrock over various length dimensions. To address this problem, collaborative investigations coupling hydraulic, geochemical and geophysical field techniques, and interpretive methods will be conducted in the Mirror Lake drainage basin. In dense clusters of bedrock wells and drift piezometers, referred to as experimental-well fields, investigations of fluid movemen and chemical transport will be conducted over distances tha range from a few meters to 150 m. To investigate fluid movement and chemical transport over distances that extend to the dimensions of the drainage basin, similar investigative hydrogeologic techniques will also be applied to the information collected from bedrock wells and drift piezometers distributed areally over the drainage basin. The investigations in the experimental-well fields and over the drainage basin will be coupled with geologic, lithologic, and fracture mapping data collected in boreholes and outcrops in the Mirror Lake drainage basin and the immediate vicinity. The investigation of fluid movement and chemical transport over length dimensions ranging from meters to the dimensions of the the drainage basin, will provide a means of addressing questions associated with ground-water contamination that are of importance in heterogeneous bedrock flow regimes. Over the dimensions of the experimental-well fields, methods of characterizing and predicting fluid movement and chemical transport in the vicinity of point sources of pollution can be investigated, while the effect of contamination on a regional-flow regime in a fractured formation will be investigated by the drainage-basin scale investigations.

Two experimental-well fields are planned, each containing 8 to 12 bedrock wells and 8 to 12 drift piezometers. In each of the experimental-well fields, methods of characterizing and predicting fluid movement and chemical transport over distances of less than 150 m will be conducted. Because of the spatial variability in the bedrock, the consequences of characterizing fluid movement and chemical transport from one site to the next will be assessed by comparing the success of the field techniques and interpretive methods applied at the two experimental-well fields. The location of the two experimental-well fields in the Mirror Lake drainage basin are designated as FSE and CO in figure 2. The FSE well field currently has seven bedrock well and eight drift piezometers (fig. 3), whereas the CO experimental-well field currently has two bedrock wells and two drift piezometers.

In the experimental-well fields, geology, lithology, fracture mapping, geochemistry, surface geophysics, borehole geophysics and cross-hole tomographic imaging by seismic and electromagnetic sources will be used to infer the spatial variability of hydraulic and transport properties of the bedrock. This information will be correlated with single-hole hydraulic tests that identify variability in the bedrock permeability along a given borehole, and cross-hole hydraulic tests that identify the hydraulic responses of larger sections of the bedrock. Controlled tracer experiments between boreholes separated by distances of 10 to 30 m will be conducted and correlated with the information from the other investigative techniques. The results from these field tests will be used to develop a predictive model of fluid movement and chemical transport over the dimensions of the experimental-well field. The ability to predict fluid movement and chemical transport over dimensions larger than the hydraulic and tracer tests will be assessed by conducting controlled hydraulic and tracer tests over dimensions larger than 30 m. Thus, small sections of the bedrock will be intensively tested with the intention of predicting fluid movement and chemical transport over larger dimensions. Several questions that will be addressed in the prediction of fluid movement and chemical transport over the dimensions of the experimental-well fields concern the applicability of different conceptual approaches to predict fluid movement and chemical transport in fractured rock. For example, the applicability of discrete-fracture models, distributed-parameter models, a combination of discrete-fracture and distributed-parameter models, and the introduction of geologic and lithologic data into ground-water flow models will be addressed.

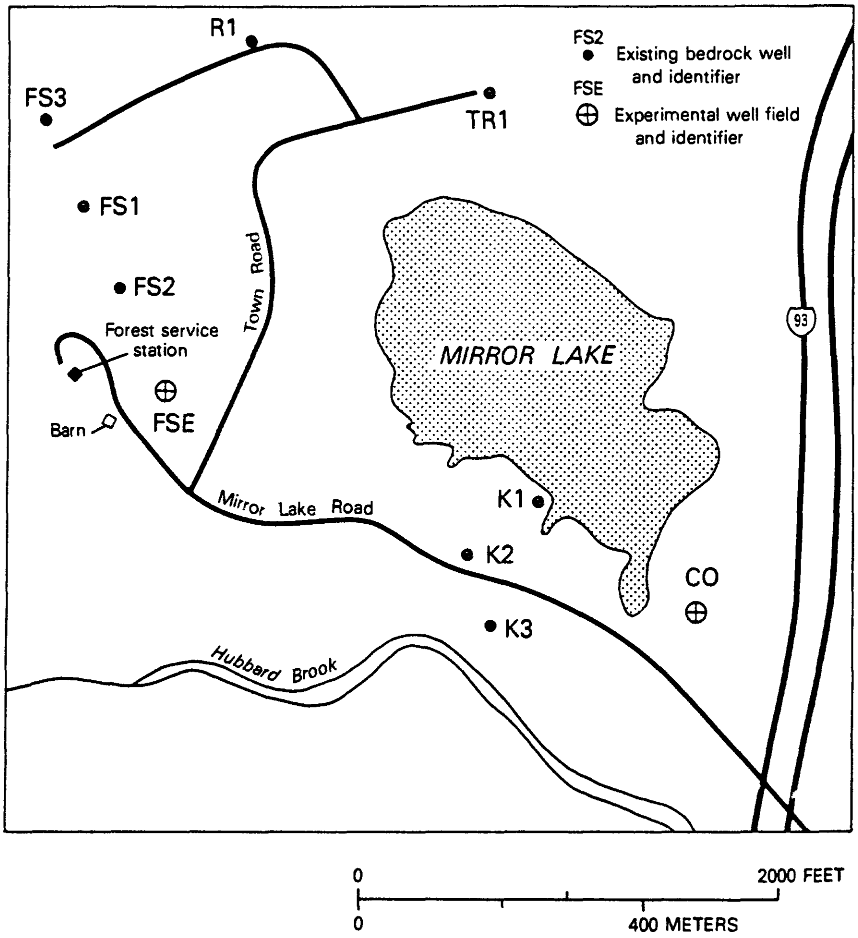

Figure 2. Map of bedrock wells and experimental-well fields in the Miror Lake drainage basin.

Bedrock wells and drift piezometers will be installed for areal coverage of the drainage basin to investigate fluid movement and chemical transport over dimensions larger than the experimental-well fields. There are currently 10 bedrock wells for areal coverage of the drainage basin, excluding the bedrock wells in the FSE and CO experimental-well fields (fig. 2). One or more drift piezometers also are in the vicinity of the bedrock wells that are areally distributed over the watershed. An additional five bedrock wells are planned for areal coverage of the Mirror Lake drainage basin.

The lithology of the bedrock in boreholes drilled for areal coverage of the drainage basin will be identified from cores or drill cuttings. Borehole geophysical logging then will be conducted to identify the location and orientation of fractures and to confirm the lithologic logs; the acoustic televiewer log identifies fractures and fracture orientation, while the natural-gamma log strongly correlates with presence of pegmatite. The water-producing fractures will be identified using a high-resolution, heat-pulse flowmeter that monitors fluid velocity in the borehole during pumping. The location of water-producing fractures is identified by changes in fluid velocity at various depths in the borehole. These geophysical logs will identify zones for more detailed hydraulic testing and geochemical sampling. Single-hole hydraulic tests (either pumping or injection testing) will be conducted to obtain a profile of hydraulic conductivity over the depth of the borehole. All sections of the borehole having fractures will be tested. In intervals where water can be withdrawn, samples will be collected for chemical and isotopic analysis. Inflatable packers then will be installed at selected depths in the borehole to hydraulically isolate intervals for monitoring hydraulic heads in the bedrock. A similar investigative approach also will be adopted for those bedrock wells drilled in the experimental-well fields.

The bedrock wells distributed in the drainage basin are separated by at least 100 m. Aquifer tests that hydraulically stress the bedrock between these boreholes will be attempted to identify bulk hydraulic properties of large sections of the bedrock. Because of the extreme spatial variability in hydraulic properties of the bedrock, controlled tracer experiments are unlikely to be successful. Therefore, transport properties of the bedrock over distances that exceed 100 m will be inferred from chemical and isotopic data, coupled with hydraulic data and results from ground-water flow and transport modeling.

The relatively small dimensions of Mirror Lake drainage basin make it possible to collect detailed hydrogeologic information over the scale of the drainage basin to develop a model of fluid movement and chemical

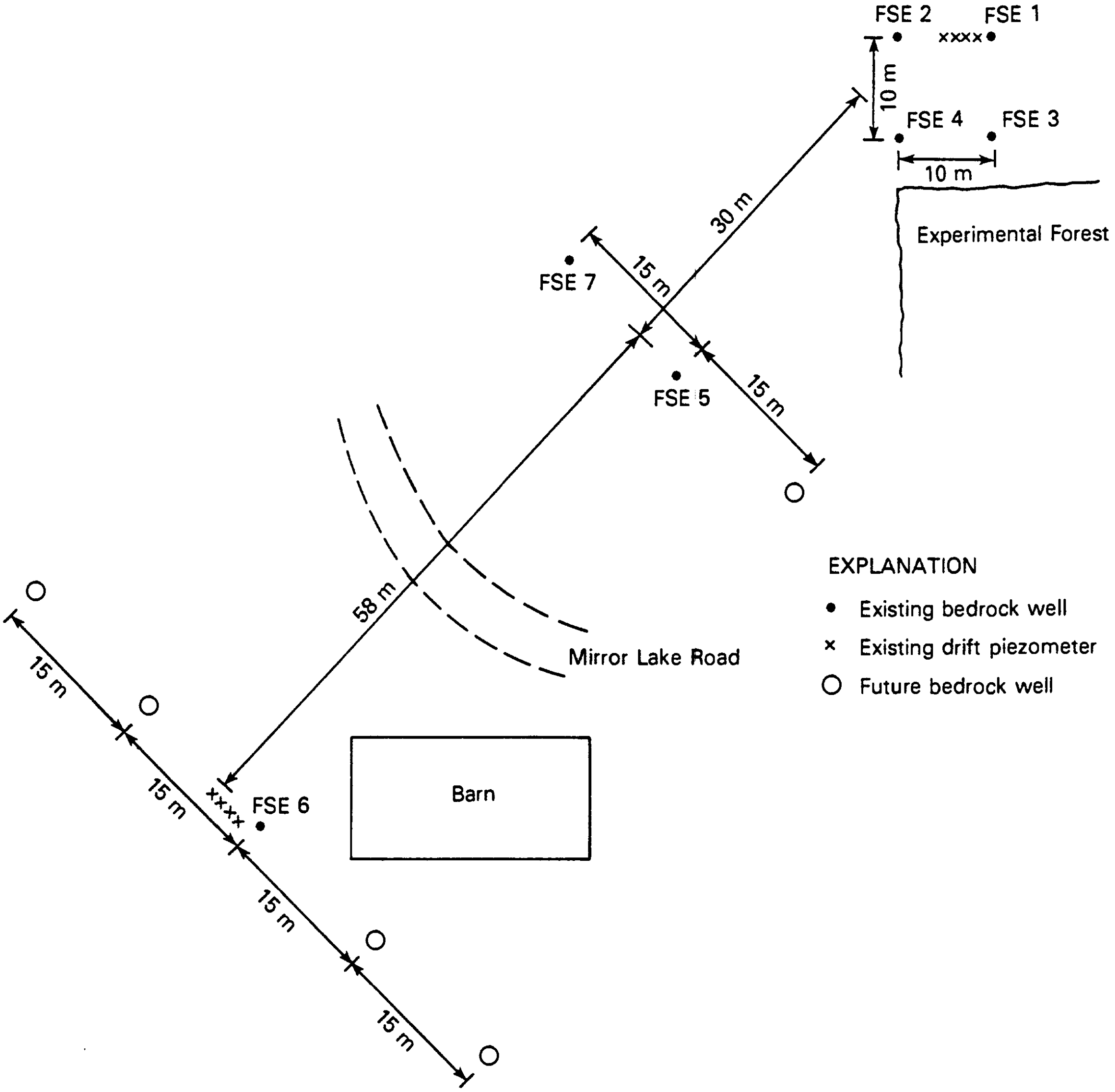
FSE 2
FSE 1
10 m
FSE 4
FSE 3
10 m
Experimental Forest
30 m
FSE 7
15 m
FSE 5
15 m
Mirror Lake Road
58 m
15 m
15 m
FSE 6
Barn
15 m
15 m
EXPLANATION
● Existing bedrock well
× Existing drift piezometer
○ Future bedrock well

Figure 3. Map of bedrock wells in the FSE experimental-well field.

transport. A water budget in the Mirror Lake drainage basin will be established on the basis of climatological data, and streamflow- and lake-discharge data. Well hydrographs in drift piezometers and bedrock wells and estimates of recharge to Mirror Lake will be used to calibrate a ground-water flow and transport model that will be further conditioned by geologic, lithologic, hydraulic, isotopic, and chemical data. Ground-water flow and chemical-transport models developed for the dimensions of the drainage basin will also address the applicability of different conceptual models of fluid movement and chemical transport in heterogeneous bedrock flow regimes, and will consider the significance of introducing geologic, lithologic, and fracture data.

SUMMARY

A multidisciplined research program in fractured-rock hydrogeology is planned in the bedrock of the Mirror Lake drainage basin in the Hubbard Brook Experimental Forest in central New Hampshire. The research program will use collaborative interpretations from a variety of hydrogeologic investigative techniques (for example, surface geophysics, borehole geophysics, seismic and electromagnetic tomographic imaging, geochemical analysis, hydraulic testing, and tracer testing) in conjunction with geologic, lithologic, and fracture mapping data. Field investigations will focus on methods of physically identifying spatial variability in hydraulic properties in heterogeneous

bedrock-flow regimes over various length dimensions. The field investigations will be augmented by the application and development of interpretive approaches to predicting fluid movement and chemical transport in heterogeneous bedrock-flow regimes over various length dimensions.

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COMPARING GEOPHYSICAL LOGS TO CORE AND CROSS-HOLE FLOW LOGGING IN THE MIRROR LAKE DRAINAGE BASIN

By F.L. Paillet[1]

ABSTRACT

An ongoing fracture-flow study based on geophysical log analysis and other geophysical and hydrologic techniques was expanded by adding additional boreholes to an existing experimental well field in the Mirror Lake watershed. One of these new boreholes was cored in order to compare lithologies and fractures identified on cores with those inferred from geophysical logs. Comparison of cores with geophysical logs confirms the accuracy of interpretation of generalized lithology and fractures on the basis of geophysical logs alone. However, the logs did not indicate some of the minor, possibly closed in-situ fractures seen in the recovered cores. At the same time, one of the largest and most permeable fractures indicated by the geophysical logs was not observed in the core. The original boreholes in the experimental well field were shown to intersect a highly conductive zone formed by the intersection of numerous discrete and discontinuous fractures. Cross-borehole pumping tests demonstrate that the highly conductive zone identified in previous studies intersects the core hole, but not the other new boreholes indicating the discontinuous and heterogeneous nature of permeable zones in bedrock at this site.

INTRODUCTION

The Mirror Lake drainage basin in the Hubbard Brook Experimental Forest in central New Hampshire (fig. 1) was selected as one of several sites for the application of borehole geophysical methods to the hydraulic characterization of fractures. This site was of interest because previous hydrologic studies indicated that fracture flow might be interacting with flow in surficial aquifers, and an ongoing aquifer-monitoring program might provide data required to interpret that interaction (Winter, 1984). Initial plans for such an effort recognized that flow systems in fractures are difficult to characterize on the basis of data obtained in a limited number of boreholes. For this reason, the early phase of the Mirror Lake hydraulic study of fractures was based on the intensive study of flow in a relatively small body of fractured rock. After the fractures in this small volume of rock were thoroughly investigated, the insights obtained in this study would be extended to a wide-scale study of boreholes in the watershed.

The proposed small-scale fracture study was begun in 1984. Existing bedrock boreholes were used at a site with relatively easy access for geophysical equipment. Additional boreholes were drilled to form a set of four boreholes that isolated a prismatic volume of rock. This rock volume is situated underneath about 50 ft (feet) of glacial drift, and has a square cross-section defined by the borehole spacing of about 30 ft on each side. Three of the boreholes were drilled to a depth of 350 ft, the fourth borehole extends to 750 ft. The boreholes are completed several feet into bedrock with steel casing, so that hydraulic heads in bedrock would be isolated from hydraulic heads in the surficial drift. Each borehole was drilled with a nominal diameter of 6 in. using conventional air-percussion methods. According to the current scheme for numbering the Mirror Lake boreholes, these boreholes (FSE-1,2,3, and 4) define the first boreholes in an expanding Forest Service East (FSE) experimental well field. This paper reviews the results from earlier fracture hydrology studies in the FSE boreholes, and integrates the geophysical and core log information obtained from a recently drilled borehole into the latest models for flow in fractured rock in the vicinty of the FSE study site.

PREVIOUS RESULTS FROM THE FSE NETWORK

During the 1984-87 field seasons, geophysical logging and other techniques were very successful in characterizing the flow system in fractures within the body of rock delimited by the first four FSE boreholes. These results are described in detail in a series of papers and reports (Paillet, 1985; Hardin and others, 1987; Paillet, Hess, Cheng, and Hardin, 1987; Paillet, Hsieh, and Cheng, 1987). The primary geophysical instrument used to identify fractures intersecting the FSE boreholes is the acoustic televiewer, which produces a photograph-like image of the borehole wall by measuring the intensity of reflection produced by a scanning ultrasonic beam. Intensive televiewer logging allowed characterization of fractures intersecting the borehole in terms of strike, dip, and relative aperture. This data indicated that the FSE boreholes are intersected by a series of generally east- and west-dipping fractures, and that the frequency of fractures decreases irregularly with depth.

Additional studies, such as high-resolution vertical-seismic profiling and packer isolation and injection tests, were used to define the hydraulic conductivity within the rock mass defined by the FSE boreholes. The results of these studies appeared to contradict the geophysical logs in that the studies indicate the presence of a highly conductive zone in the form of a single, nearly horizontal layer connecting all four boreholes at a depth of about 150 ft. This observation appears inconsistent with the televiewer and acoustic logs which indicate that permeable fractures are distributed along the boreholes, and that most of these fractures dip at angles greater than 40 degrees from the horizontal. The apparent contradiction was resolved by the application of cross-borehole flow logging using a recently developed, high-resolution flowmeter (Hess, 1982; 1986). Measurement of the flows induced in three FSE boreholes by pumping in the fourth indicated that flow entered and exited boreholes through steeply dipping fractures, each of which intersected the boreholes in the 145 to 155 ft depth interval. These results and the fact that fractures clearly did not project from one FSE borehole to another demonstrate that

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[1]U.S. Geological Survey, Denver, Colo.

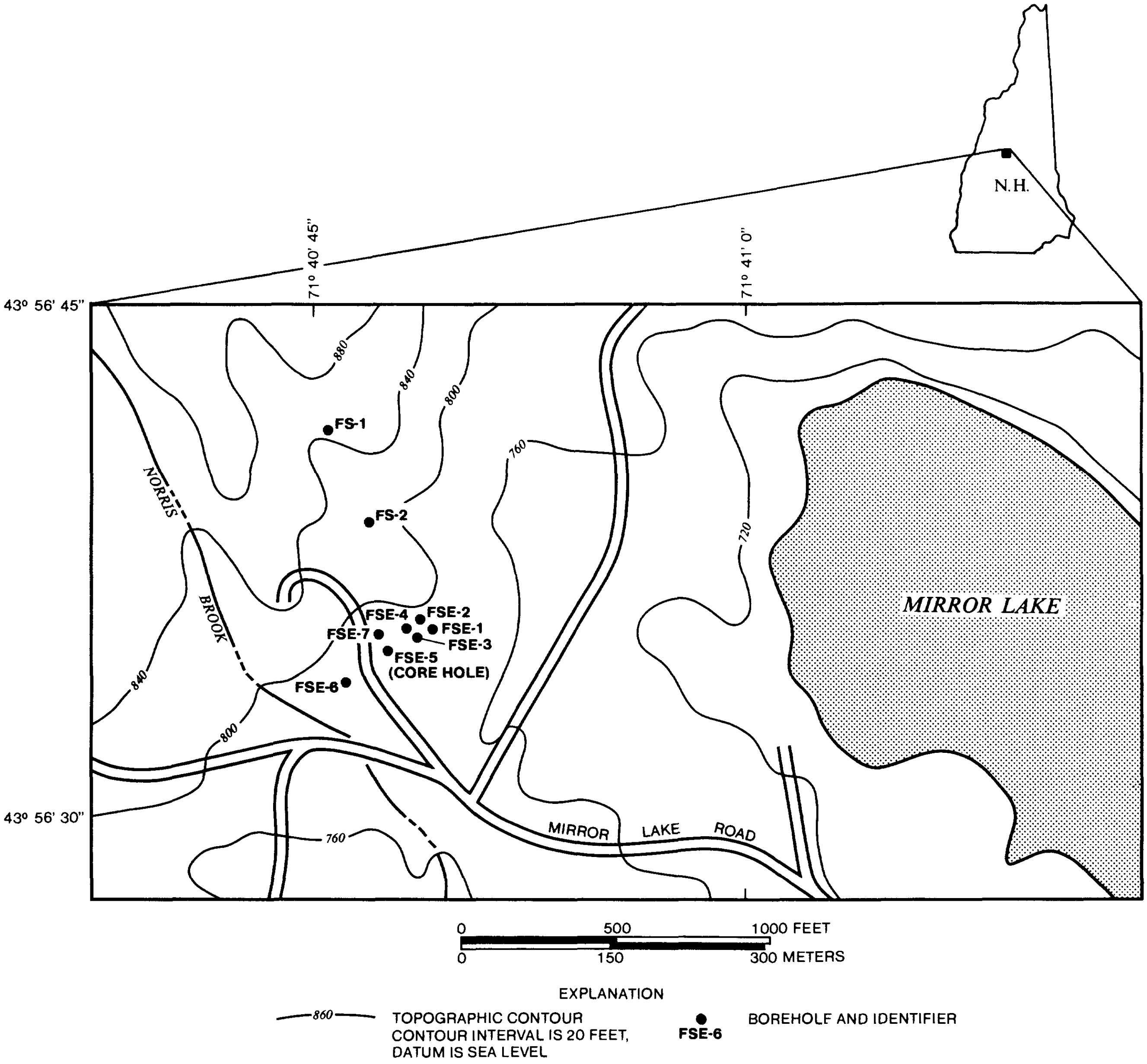
N.H.
43° 56' 45"
43° 56' 30"
71° 40' 45"
71° 41' 0"
880
840
800
760
720
FS-1
FS-2
FSE-4
FSE-2
FSE-7
FSE-1
FSE-3
FSE-5
(CORE HOLE)
FSE-6
NORRIS BROOK
MIRROR LAKE
MIRROR LAKE ROAD
0 500 1000 FEET
0 150 300 METERS
EXPLANATION
860 TOPOGRAPHIC CONTOUR
CONTOUR INTERVAL IS 20 FEET,
DATUM IS SEA LEVEL
FSE-6 BOREHOLF AND IDENTIFIER

Figure 1. Location of the Forest Service East (FSE) and Forest Service (FS) series boreholes at Mirror Lake, New Hampshire.

the large-scale, nearly horizontal conductive zone consists of discontinuous intersecting, steeply dipping fractures.

EXPANSION OF THE BOREHOLE NETWORK

The insights obtained from the first FSE borehole studies seemed to establish the basis for a conceptual model of flow in fractures in the Mirror Lake watershed. The fracture system is conceptualized as an irregular distribution of discontinuous east- and west-dipping fractures, the almost random intersections of which defined larger-scale permeable zones. One of these zones was present in the area covered by the original FSE network. The next step in the Mirror Lake fracture study was to consider a scale of investigation larger than that given by the 30 ft separation of the FSE boreholes. This larger-scale investigation was to consider hydraulic response between boreholes separated by about 300 ft. The new borehole, FS-2, and an existing, deepened borehole, FS-1, are shown in figure 1. These boreholes were located on the assumption that topography controlled the larger-scale flow paths, and they were spaced to increase the scale of investigation by an order of magnitude (Paillet and Kapucu, 1989).

The larger-scale study of flow in fractures at Mirror Lake was designed to investigate how the permeable zone in the FSE network was related to larger-scale flow systems. The expanded study was designed to investigate these interconnections by a larger-scale cross-borehole flow logging study where water levels would be drawn down in one of the FSE boreholes for a prolonged period. The first indication that the preliminary fracture flow model was inadequate, and that the proposed flowmeter study would not go as planned, was given by the extended period required for borehole FS-2 to fill with water 5 days after drilling; this indicated that bedrock had low permeability near this borehole. At the same time, the televiewer logs indicated that borehole FS-2 intersected several intensely fractured intervals, so that low fracture frequency alone could not explain the negligible flow of ground water in the borehole.

The larger-scale cross-borehole experiment produced a completely negative result. The prolonged drawdown of borehole FSE-4 produced less than 0.5 ft of drawdown in boreholes FS-1 and FS-2 in the first day of the test, and this drawdown began to decrease thereafter in borehole FS-2. This result indicated that the permeable zone defined by the FSE boreholes was not connected to the fractures that intersected boreholes FS-1 and 2. Research plans were modified to include systematic expansion of the FSE network to delineate the dimensions of the permeable zone at 150 ft in depth, and to define how this zone may be integrated into a large-scale fracture-flow system at scales intermediate between the 30 ft and 300 ft separation of the two previous experiments.

THE NEW CORE HOLE- -BOREHOLE FSE-5

The FSE network was expanded by drilling the FSE-5 core hole, and then drilling two additional boreholes (FSE-6 and 7) and reaming the cored borehole, FSE-5, to the standard 6-in. diameter, in 1989 (fig. 1). The small diameter of the core hole and time constraints restricted logging in 1989. As a result, only caliper and televiewer logs were obtained in the 3-in. diameter core hole. Televiewer log quality was degraded because the small borehole diameter made it difficult to separate the amplitude of the source pulse from that of the reflected signal. In 1990, a full suite of geophysical logs (caliper, temperature, natural gamma, neutron, single-point resistivity, and televiewer) were run in the reamed core hole. These logs were expected to be more useful than those obtained in the original core hole in relating core observations to log data because the larger diameter and rougher wall of the reamed borehole would be analogous to borehole conditions in other bedrock boreholes.

The core intervals were described and photographed as they were removed from the core barrel. Recovery was generally 100 percent, with the exception of the core recovered from the interval between 110 and 120 ft in depth, where the core was fragmented and about 10 percent of the total cored interval was missing. General core lithology consists of a weakly foliated granite extending from bedrock surface at a depth of about 54 ft to contact with an interval of interfingered pegmatite and granite at about 150 ft. The pegmatite and granite continues to the total depth of the core at about 200 ft. A listing of the fractures identified on the core is given in table 1. The core appeared to sample a representative population of fractures. Many of these showed extensive halos of alteration and mineral staining of grain surfaces near fracture faces.

COMPARISON OF CORE FRACTURES WITH TELEVIEWER AND OTHER LOGS

One of the primary objectives of the coring was to compare the identification of lithology and fractures on core with the interpretation of lithology and fractures based on geophysical logs. The suite of geophysical logs run in the core hole is shown in figure 2. A summary of interpretations related to core observations and known geophysical log responses in crystalline rocks is given in table 2. In general, the logs express lithology by indicating the contact between the granite and the pegmatite and granite intervals (gamma, caliper, and neutron logs), and by indicating the alteration associated with some of the major fractures (neutron log). One important result of the log analysis is the indication of a contrast in solute content of the standing water column near 140 ft. The resistivity log indicates that water above this depth is somewhat fresher (more resistive) than water below this depth. This could be an indication that ground water is entering the borehole near the bottom of casing and exiting at one of the fractures indicated on the televiewer log in the 140 to 145 ft depth interval.

One of the most important results of the core analysis is a comparison between fracture identification using the televiewer log and fractures identified on core. A comparison between core and televiewer fracture data is given in table 1. These comparisons are based on televiewer logs made in the core hole. The smooth walls of the core hole made fractures easier to detect than the fracture images in the rough-walled borehole after reaming. Although the small core-hole diameter limited azimuthal coverage of the borehole wall, the limited azimuthal coverage did not prevent the detection of relatively minor fractures. The one outstanding difference between the core observations and televiewer interpretations is that the core observations failed to identify a major fracture near 113 ft in depth, where there was considerable core loss. The televiewer log image of this fracture in the reamed core hole is given in figure 3A. Although the core was fragmented and damaged in drilling, there were no observations of altered rock to indicate that the observed breaks in core were not drilling induced. The televiewer image of another major fracture is compared to the core photograph in figure 3B. This televiewer log shows an unexpected result from the core hole reaming. The drill bit apparently did not remain centralized over the core hole during reaming, so that part of the original core hole remains embedded in the wall of the borehole. The dip and general character of the fracture image in the televiewer log is consistent with the dip of the fracture and general fracture appearance observed on the core.

A more general comparison of the quality of fracture interpretation using televiewer logs is indicated by comparing the core photographs of a number of different fractures of various sizes and orientations with the corresponding televiewer logs in both the original and reamed core hole. The results of such a study are shown in figure 4. Comparison of the original televiewer image, televiewer interpretation, and core photographs indicates that two of the three fractures in a 5-ft interval are identified in the interpretation of the reamed core hole log, but a third, smaller fracture was not detected. This minor fracture was detected in the televiewer log of the smooth-walled core hole, but televiewer-log analysis at Mirror Lake is generally applied to boreholes with rough walls produced by air-hammer drilling, similar to the rough walls of the reamed core holes. Examination of the reamed core-hole televiewer image indicates that a very faint feature is present in the image, but there is no clear fracture signal, and this faint feature would never be distinguished from foliation or borehole wall roughness on the basis of televiewer data alone. This undetected fracture does not appear to be associated with alteration and may be effectively closed.

Table 1. *Listing of fractures in core from borehole FSE-5 and comparison of core fractures to those identified using the televiewer*

[Ft, feet; --, indicate no data]

Fracture type[1]	Fracture depth on core (ft)	Televiewer match[2]	Televiewer depth (ft)	Length of intersection in core[3] (ft)	Length of intersection televiewer log (ft)	Fracture strike[4]	Fracture dip[4]
NF	61.85	A	61.50	0.15	0.25	70°	45° SE
NF?	66.95	A	66.4	0.12	.14	90°	30° S
--	--	D	68.20	--	.25	36°	45° SW
NF	71.00	B	--	.05	--	--	--
NF	71.20	B	--	.25	--	--	--
NF	74.50	A	74.10	.10	.21	45°	40° SW
NF	82.05	C	--	--	--	--	--
NF	83.30	A	82.80	.15	.25	72°	45° SE
NF	83.95	A	83.50	.25	.54	45°	65° SE
NF	84.30	B	--	--	--	--	--
CF	84.50	C	--	.04	--	--	--
NF	84.60	C	--	.03	--	--	--
NF	85.35	A	84.90	.04	<.20	--	<20°
NF	90.06	C	--	.10	--	--	--
NF	91.48	A	90.00	.13	.21	0°	40° W
NF	93.36	A	92.80	.08	.09	20°	20° SW
NF	93.76	A	93.20	.08	.09	0°	20° W
NF	94.99	A	94.60	.05	.09	0°	20° W
NF	95.23	B	--	.08	--	--	--
NF	95.42	B	--	.07	--	--	--
NF?	96.50	C	--	.08	--	--	--
CF	96.90	C	--	.12	--	--	--
NF	97.05	B	--	.25	--	--	--
NF	97.22	A	96.70	.15	.25	54°	45° NW
CF	101.20	A	100.70	.28	.40	30°	60° NW
NF	105.77	A	105.20	.11	.14	170°	30° W
NF	106.15	A	105.60	.06	.10	180°	20° W
NF	107.35	A	106.90	.08	.10	180°	20° W
NF	109.89	A	109.40	.30	.55	55°	65° NW
--	--	D	113.20	--	.10	180°	20° W
DF	119.25	C	--	<.02	--	--	--
DF	124.65	A	123.75	.05	.10	18°	25° NW
CF	126.08	C	--	.18	--	--	--
CF	127.52	C	--	.18	--	--	--
--	--	D	127.85	--	.20	63°	40° SE
CF	128.57	A	128.10	.18	.35	90°	55° S
NF?	129.78	C	--	.22	--	--	--
NF	135.68	A	135.10	.00	<.05	--	--
NF	135.71	B	--	.00	--	--	--
NF	135.76	B	--	.00	--	--	--
NF	135.86	B	--	.03	--	--	--
CF?	135.98	C	--	.04	--	--	--
CF	135.99	C	--	.04	--	--	--
NF	136.58	A	136.25	.02	<.05	--	--
CF	136.76	B	--	--	--	--	--

Table 1. *Listing of fractures in core from borehole FSE-5 and comparison of core fractures to those identified using the televiewer--Continued*

[Ft, feet; --, indicate no data]

Fracture type[1]	Fracture depth on core (ft)	Televiewer match[2]	Televiewer depth (ft)	Length of intersection in core[3] (ft)	Length of intersection televiewer log (ft)	Fracture strike[4]	Fracture dip[4]
NF	137.09	B	--	--	--	--	--
NF	137.13	B	--	--	--	--	--
CF	137.20	B	--	--	--	--	--
NF	138.95	B	--	--	--	--	--
DF?	140.70	A	139.90	--	.35	45°	55° SE
--	141.00	B	--	--	--	--	--

[1] Fracture types.

NF = naturally open fracture
CF = sealed, mineralized fracture
DCF = CF opened by drilling
DF = break probably produced during drilling

[2] Fracture match code.

A = positive match
B = fracture may be present but cannot be definitely identified on televiewer log
C = does not appear to be anything on televiewer log
D = definite fracture on televiewer log with no corresponding core feature

[3] Because of difference between core and borehole diameter, height of intersection on televiewer log should be about twice that on core for the same dip.

[4] Determined from televiewer data.

CROSS-HOLE FLOW LOGGING IN THE NEW FSE BOREHOLES

One of the primary objectives in the drilling of the additional FSE boreholes was the tracking of the highly conductive zone at about 150 ft in depth found to connect the original four FSE boreholes. Cross-hole pumping tests were conducted in 1990. The highly conductive zone in the original network was found to intersect borehole FSE-5, but not boreholes FSE-6 and FSE-7. Pumping at a rate of about 5 gallons per minute from borehole FSE-4 produced measurable flows in borehole FSE-5, but produced negligible drawdown in the other new boreholes. In the original cross-borehole tests, discharge from borehole FSE-4 was found to produce flow in the other FSE boreholes within 10 seconds after the pump was started. In the flowmeter tests conducted in 1990, flow was first detected in borehole FSE-5 18 seconds after pumping was started in borehole FSE-4. On the basis of these results, the main highly conductive zone intersects borehole FSE-5, where the zone has about the same permeability as the zone intersected by the original FSE array; however, the zone does not intersect boreholes FSE-6 and FSE-7.

The flow regime induced in borehole FSE-5 during the cross-hole pumping tests is shown in figure 5. The data show that, when water is removed from the fracture zone by pumping from borehole FSE-4, water is removed from storage in borehole FSE-5, exiting primarily by means of the large fracture at a depth of 133 ft; additional outflow occurs between 135 and 140 ft in depth. The lowermost exit point corresponds to the shift in the resistance log shown in figure 1, confirming the interpretation of this depth as an outlet for downward-circulating water. During the later stages of the cross-borehole test, the water coming from storage in casing was augmented by inflow in the 90- to 100-ft depth interval. These results are integrated into the results from the original FSE cross-hole flowmeter tests shown in figure 6. The figure shows that the highly conductive zone dips at a shallow angle toward the northeast, and generally is continuous between boreholes FSE-5 and FSE-4.

SUMMARY

The expansion of the FSE borehole network and the comparison of fracture characterizations based on core inspection with those based on geophysical log analysis have improved our understanding of fracture permeability and ground-water circulation through fractures in at least a small part of the Mirror Lake watershed. Geophysical logs including gamma, neutron, and single-point resistivity logs appear effective in delineating contacts between major lithologies, and comparison of logs with core generally confirm the lithologies interpreted on the basis of geophysical logs alone in other Mirror Lake boreholes. The core data also generally confirm the effectiveness of televiewer logs and other geophysical data in characterizing major, permeable fractures, although the televiewer may not be able to resolve some of the minor, possibly closed fractures intersected by the borehole. Distinguishing such minor fractures from foliation and borehole-wall roughness will continue to be a problem in televiewer-log interpretation at Mirror Lake.

The results of the latest cross-borehole flow measurements provide additional information about hydraulically conductive zones that define patterns of ground-water flow in fractures. The latest results from the new FSE boreholes indicate that the conductive zone encountered by the first four FSE boreholes has very sharp boundaries. The zone intersects borehole FSE-5 where permeability is nearly the same as that measured in the original network, but the zone seems nearly impermeable in the rocks between borehole FSE-5 and the other new boreholes. The latest data support

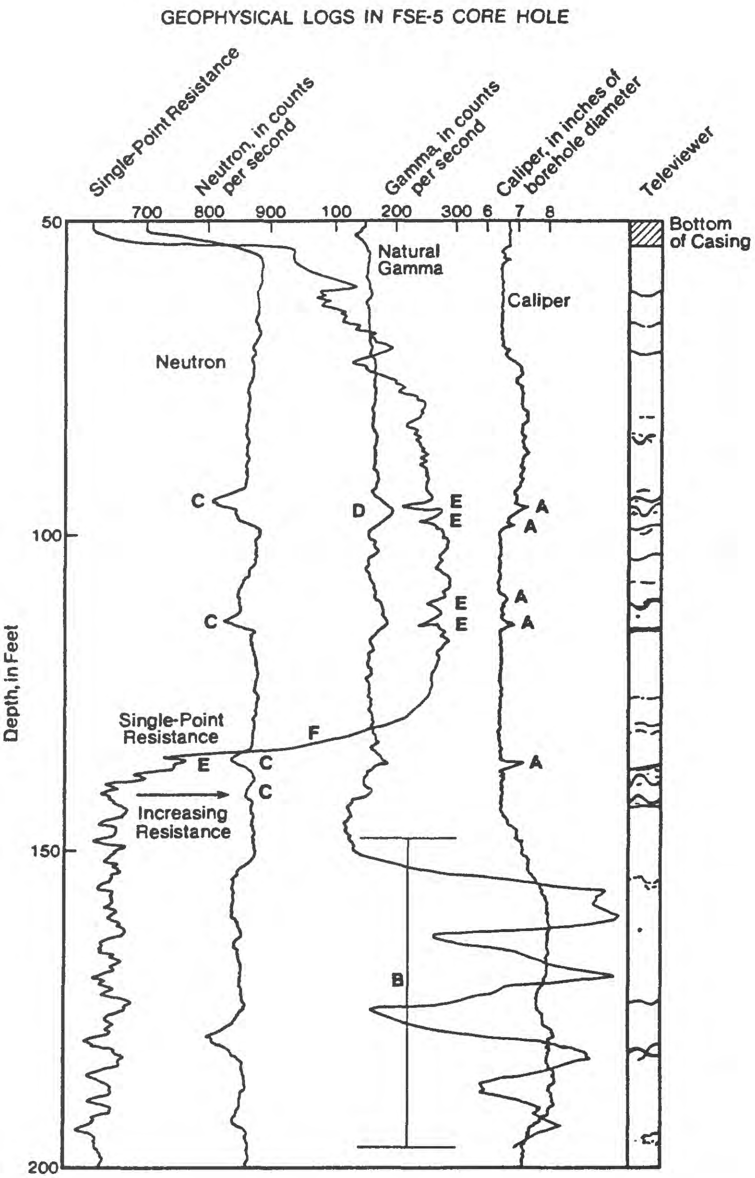

Figure 2. Composite of single-point resistance, neutron, natural gamma, caliper, and televiewer logs for the FSE-5 core hole; letters A-F denote features discussed in table 2.

Table 2. *Comments on geophysical log interpretation for core hole FSE-5*

Log annotation	Interpretation
A	Sharply defined borehole enlargements are associated with drilling damage and washout of alteration products at the mouths of major fractures.
B	Significant increase in natural gamma activity is associated with natural radioisotope concentrations in pegmatite.
C	Local anomalies on the neutron log correspond to the presence of alteration clays associated with some of the major fractures.
D	Small gamma anomaly may indicate slight radioisotope concentration by precipitation from ground water associated with major fracture zone.
E	Local low-resistance anomalies on the single-point resistivity logs result from the combination of local borehole enlargement and presence of alteration clays in major, permeable fractures.
F	Shift in single-point resistance log probably indicates contact between different water qualities in the fluid column filling the borehole.

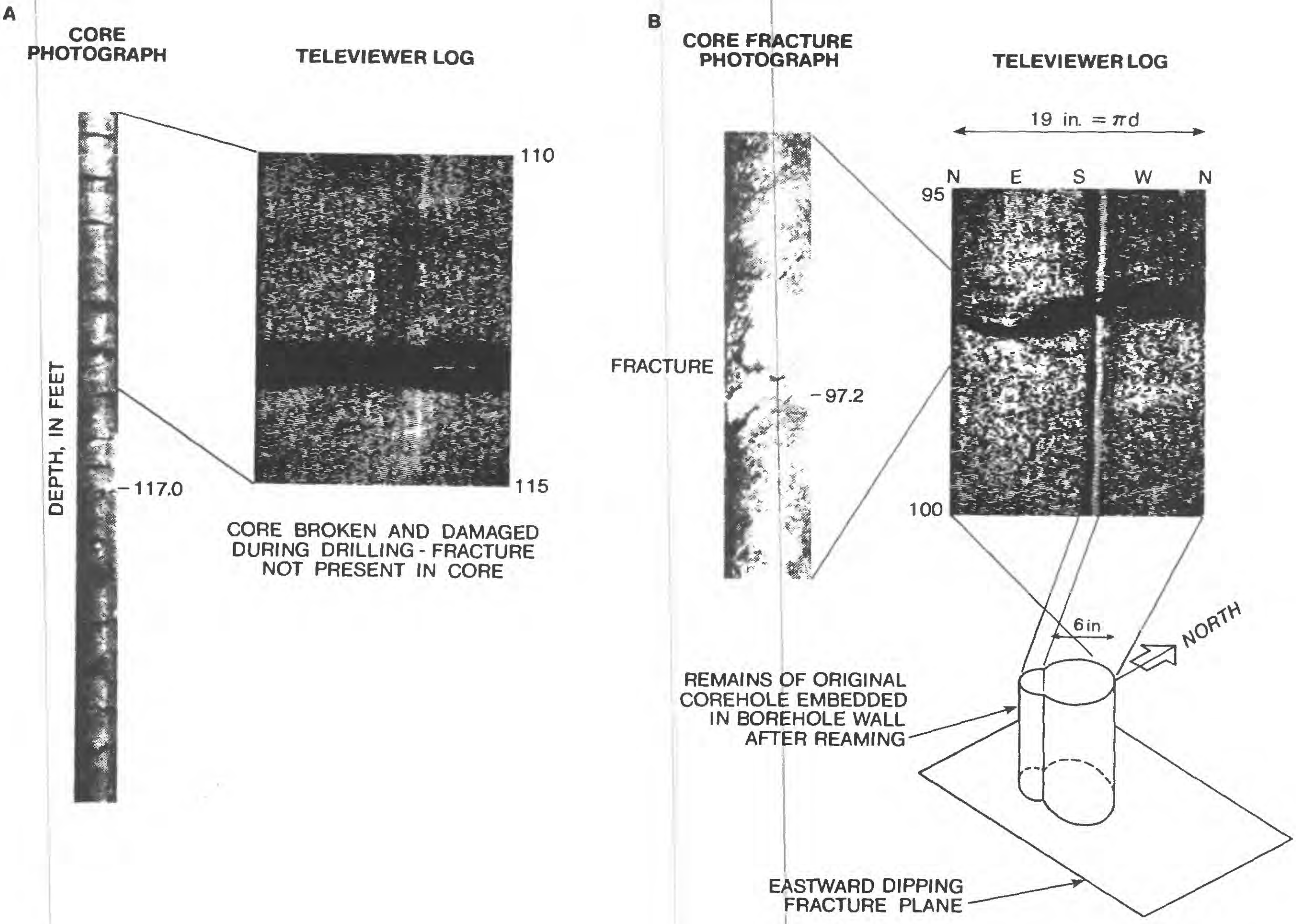
A
CORE PHOTOGRAPH
TELEVIEWER LOG
110
115
DEPTH, IN FEET
-117.0
CORE BROKEN AND DAMAGED DURING DRILLING - FRACTURE NOT PRESENT IN CORE
B
CORE FRACTURE PHOTOGRAPH
TELEVIEWER LOG
19 in. = πd
N
E
S
W
N
95
100
FRACTURE
-97.2
6 in
NORTH
REMAINS OF ORIGINAL COREHOLE EMBEDDED IN BOREHOLE WALL AFTER REAMING
EASTWARD DIPPING FRACTURE PLANE

Figure 3. Examples of televiewer log interpretation based on comparison of televiewer images with core photographs: (A) Major fracture indicated on televiewer but not on core and probably contained in interval of lost core; (B) Major fracture clearly corresponding to major fracture indicated in core.

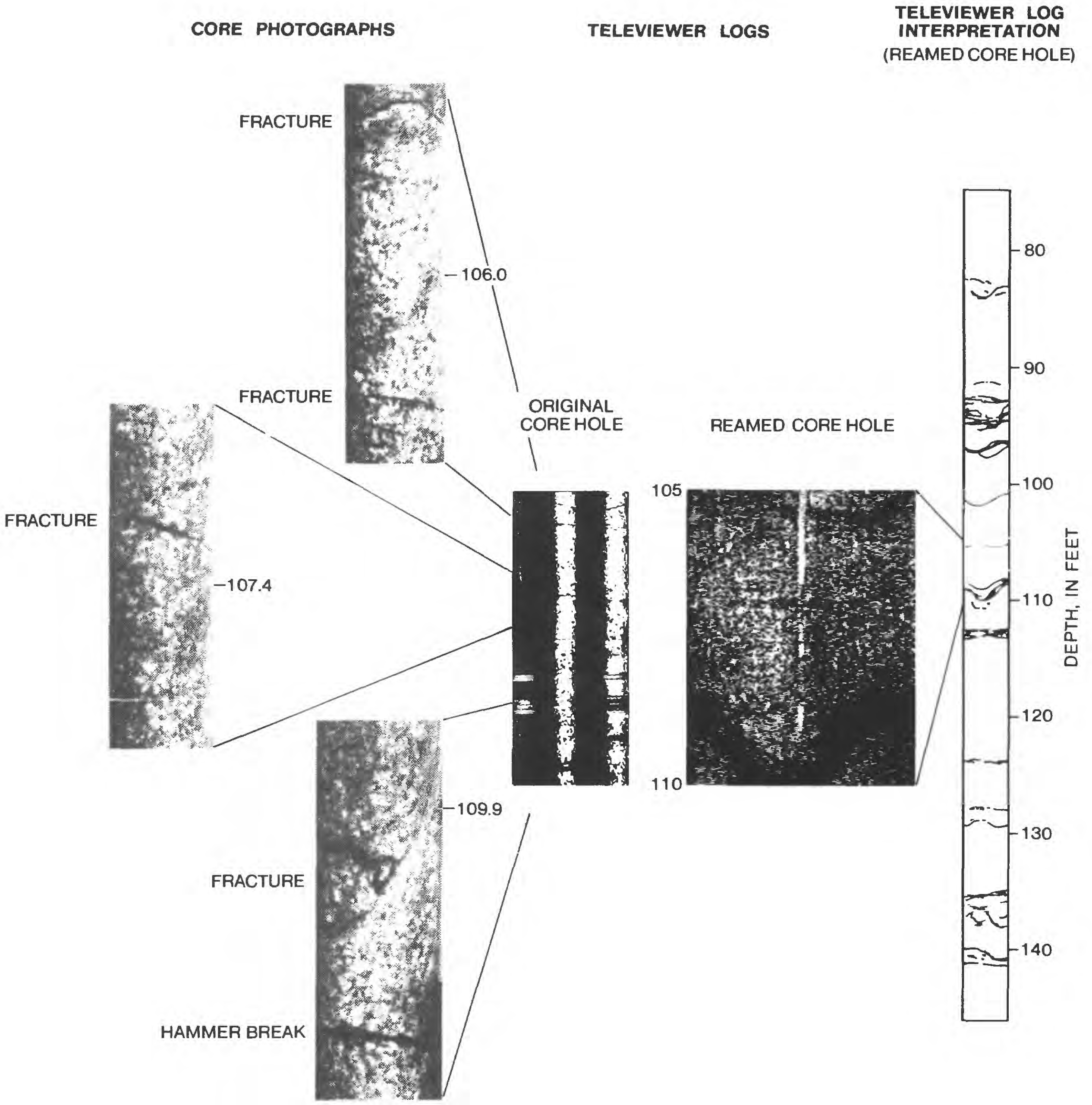
CORE PHOTOGRAPHS
TELEVIEWER LOGS
TELEVIEWER LOG
INTERPRETATION
(REAMED CORE HOLE)
FRACTURE
—106.0
FRACTURE
FRACTURE
—107.4
ORIGINAL
CORE HOLE
REAMED CORE HOLE
105
110
—109.9
FRACTURE
HAMMER BREAK
80
90
100
110
120
130
140
DEPTH, IN FEET

Figure 4. Large, intermediate, and small fractures evident in core photographs with the corresponding interval of televiewer log, illustrating the relation between the size of core fractures and extent of associated alternation with televiewer log representation.

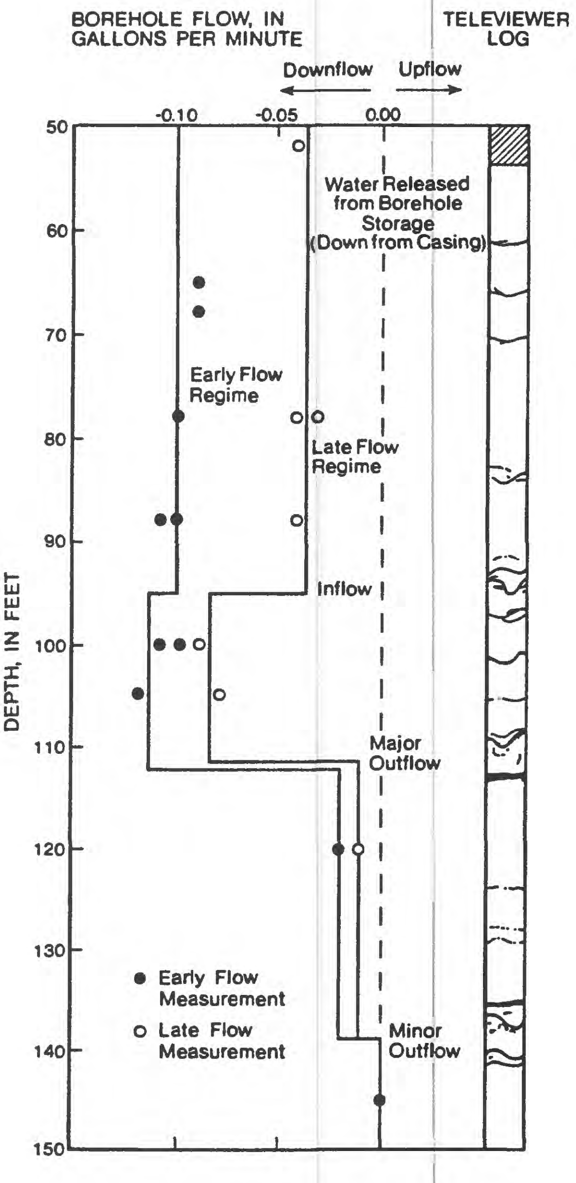

Figure 5. Vertical flow distribution measured in the core hole FSE-5 during cross-hole pumping tests.

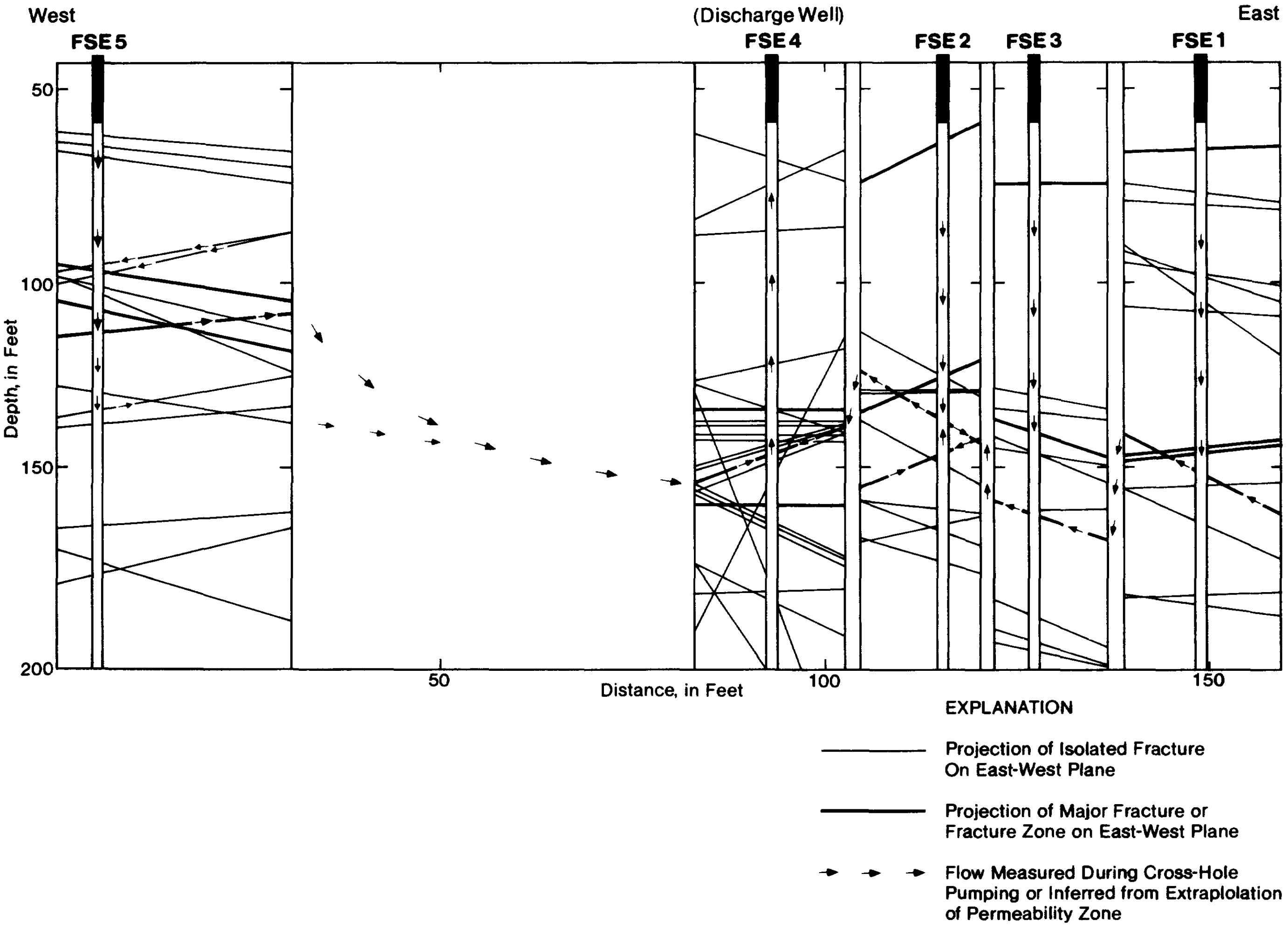
West
(Discharge Well)
East
FSE5
FSE4
FSE2
FSE3
FSE1
50
100
150
200
Depth, in Feet
50
Distance, in Feet
100
150
EXPLANATION
Projection of Isolated Fracture On East-West Plane
Projection of Major Fracture or Fracture Zone on East-West Plane
Flow Measured During Cross-Hole Pumping or Inferred from Extraplolation of Permeability Zone

Figure 6. Flow measurements in the core hole FSE-5 and flow distribution in other FSE boreholes during cross-hole pumping tests; borehole FSE-4 is the discharge well.

the model that conductive zones are the large-scale result of interconnections between short, discontinuous segments of permeable fractures. All of these results highlight the complexity of flow systems in fractures at Mirror Lake and other crystalline rock research sites, and emphasize the importance of studying fracture flow at multiple scales of investigation.

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Winter, T.C., 1984, Geohydrologic setting of Mirror Lake, West Thornton, New Hampshire: U.S. Geological Survey Water-Resources Investigations Report 84-4266, 61 p.

EXAMINATION OF HEAD DATA IN A FRACTURED AND LAYERED SYSTEM, ROCK SPRINGS, WYOMING

By Kathy Muller Ogle[1]

ABSTRACT

The White Mountain in-situ oil-shale retort area was a U.S. Department of Energy test site for burning oil shale in place to evaluate methods of oil extraction without removal of the shale. The area is 7.5 miles west of Rock Springs, Wyoming. The Tipton Shale Member of the Green River Formation (Eocene) at site 9 in the White Mountain area was retorted in 1976 to extract oil.

Head values indicate a complex ground-water flow system at White Mountain area in the vicinity of site 9. Annual temporal head fluctuations of 5 to 10 feet were observed in monitoring wells completed in four stratigraphic intervals. The potential for flow to the 10-foot-thick Tipton layer, correlating to the lower one-third of the retort chamber, from the overlying 8-foot-thick sandstone layer, is indicated by differences in head. Spatial variability indicates a potential for horizontal flow to the southwest and west within the 10-foot-thick Tipton Shale Member layer. The causes of the fluctuations in head have not been determined. However, a dynamic system is indicated by the head data.

INTRODUCTION

The White Mountain *in-situ* oil-shale retort area is 7.5 miles west of Rock Springs, Wyo. (fig. 1). Oil shales within the Tipton Shale Member of the Green River Formation (Eocene) in this area contain from 5 to nearly 50 gallons of oil per ton of shale (Lidstone and Anderson, Inc., written commun., 1989). At the White Mountain area, the Tipton lies at a depth from 25 to 120 ft (feet) beneath the surface and is 150 ft thick (Lidstone and Anderson, Inc., written commun., 1989). Ten *in-situ* oil-shale retort tests were conducted by the Laramie Energy Technology Center, Bartlesville Energy Center, and Sandia Laboratories for the U.S. Department of Energy at the White Mountain area (H.C. Carpenter, written commun., 1988). The formation at site 9 (fig. 1) was hydraulically fractured, then retorted during 1976. The oil shale in the retort chamber was ignited on April 5, 1976, and formation temperatures indicate the retorting ceased after 200 days (Glover, 1988, p. 2). Water

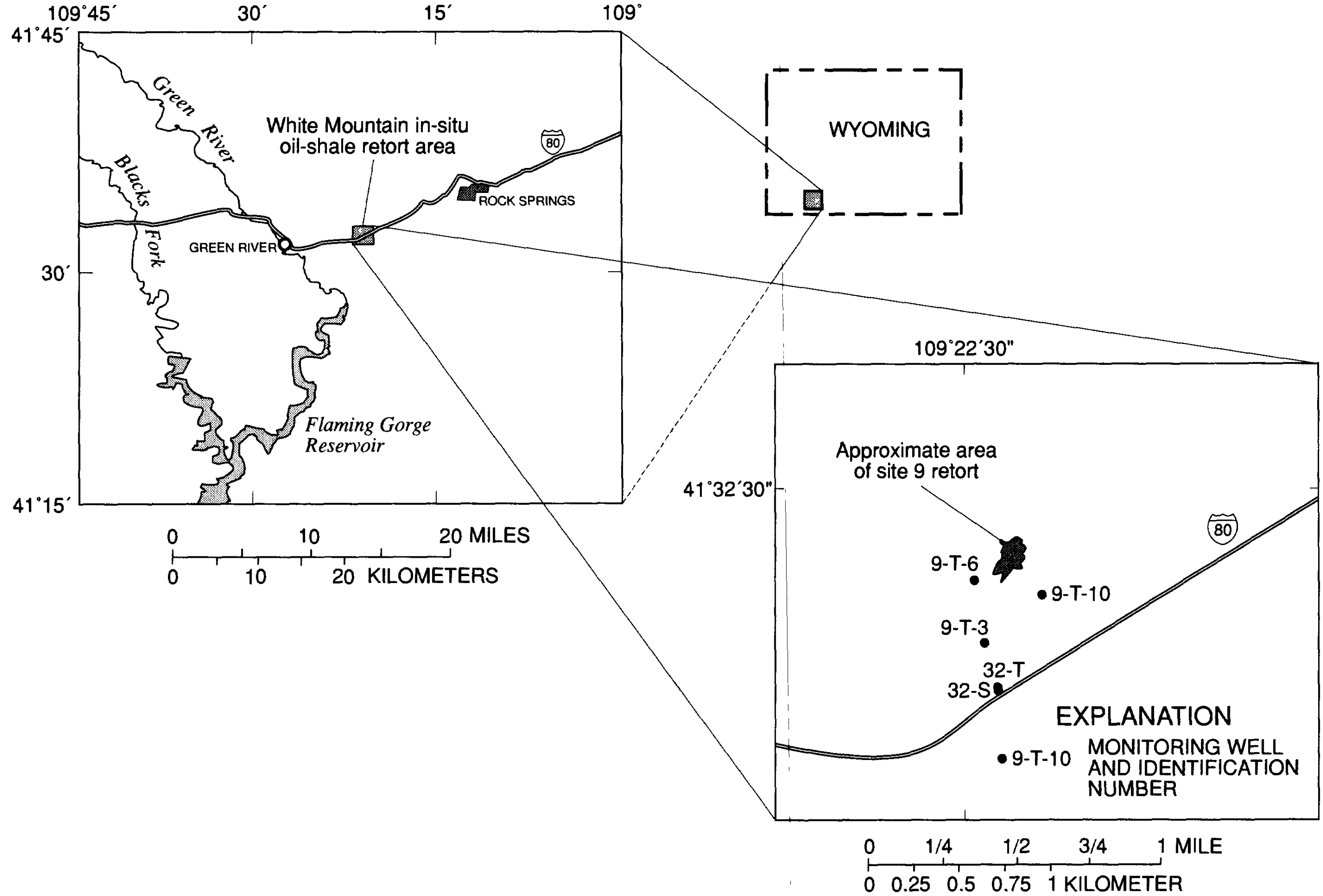
109°45′
30′
15′
109°
41°45′
30′
41°15′
Green River
Blacks Fork
White Mountain in-situ oil-shale retort area
80
ROCK SPRINGS
GREEN RIVER
Flaming Gorge Reservoir
0 10 20 MILES
0 10 20 KILOMETERS
WYOMING
109°22′30″
41°32′30″
Approximate area of site 9 retort
9-T-6
9-T-10
9-T-3
32-T
32-S
80
EXPLANATION
• 9-T-10 MONITORING WELL AND IDENTIFICATION NUMBER
0 1/4 1/2 3/4 1 MILE
0 0.25 0.5 0.75 1 KILOMETER

Figure 1. Location of White Mountain *in-situ* oil-shale retort area.

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[1] U.S. Geological Survey, Cheyenne, Wyo.

samples from the retort chamber and a number of monitoring wells at site 9 contained elevated levels of organic and inorganic compounds.

The water quality of the retort chamber and surrounding area have been the subject of several studies. Researchers have examined particular aspects of the *in-situ* retorting process, geohydrologic conditions at the site, and chemicals produced by the retorting process. EG&G WASC, Inc. (written commun., 1988) compiled a bibliography of 91 publications of studies at the White Mountain area.

The head values for selected wells completed at different depths at site 9 are examined in this paper. Head values indicated whether a hydrologic system is static or dynamic. The state of the hydrologic system is important because the ground water and any associated compounds would have a greater potential to move in a dynamic system than in a static one.

METHODS AND DATA

A static system is defined as a system with no flow and a dynamic system is defined as a system where flow occurs. In this paper, it is assumed the water-bearing units have sufficient permeability to allow flow, and the existence of a static or dynamic state is only dependent on head gradient. Fluctuations in head over time at a single well or spatially within a single unit are indicative of a dynamic system. If no temporal changes in head were observed, then it would not be possible to differentiate between a steady-state system, where inflow equaled outflow, and a static system. If no changes in head were observed spatially, a static system would be indicated. However, differences in head spatially would indicate a dynamic system.

Wells at site 9 are completed in different intervals of the water-bearing units. The differences in completion allow the head values to be examined vertically and horizontally. Four intervals were examined: (1) the overlying 8-ft-thick sandstone layer, (2) a combination of the overlying 8-ft-thick sandstone layer and the upper one-third of the Tipton Shale Member, (3) a combination of the overlying 8-ft-thick sandstone layer and the upper two-thirds of the Tipton, and (4) a 10-ft-thick Tipton layer that correlates with the lower one-third of the retort chamber.

Head data are available from the combination wells from two different study periods--1981-82 and 1989-90. These wells were used to examine temporal changes for the two periods and to examine general changes at site 9 over a 7-year period. Paired wells (located within 10 ft of each other at land surface) that were completed in the overlying 8-ft-thick sandstone layer and the 10-ft thick Tipton Shale Member layer were installed in 1989 (J.B. Lindner-Lunsford and others, U.S. Geological Survey, written commun., 1990). They were used to examine temporal changes over a 1-year period and the differences in vertical heads. Wells completed in the 10-ft thick Tipton layer were used to examine the difference in head horizontally.

To avoid short-term perturbations caused by retorting, head data collected 5 and 13 years after completion of the retorting were used in this analysis. Historical (1981-82 and 1989) head data were selected for analysis. An additional 117 head measurements were collected in April, May, and June 1990. Monthly in 1990, head data were collected in a 2-day period. Measurements at each well were repeated until two measurements were within 0.02 ft.

ANALYSIS

Wells were separated into groups based on the interval monitored. Then, head changes for the different zones were analyzed temporally and spatially.

Head values for individual wells indicate temporal fluctuations. The head values for 1981-82 and 1989-90 for three selected wells are shown in figure 2. Two wells are completed in a combination of the overlying 8-ft-thick sandstone layer and the upper one-third of the Tipton Shale Member, and one well is completed in a combination of the 8-ft-thick sandstone layer and the upper two-thirds of the Tipton. Head fluctuates about 10 ft annually. The changes in head do reflect a similar pattern, although they are not identical. Likewise, the heads of two paired wells shown in figure 3 indicate a fluctuation of about 5 ft in 1 year.

Head data indicate the potential for vertical and horizontal flow. The relations between the heads vertically were examined using paired wells at site 9. An example of the head vertically is given in figure 3. Well 32-S is completed in the 8-ft-thick sandstone layer overlying the Tipton Shale Member, and well 32-T is completed 20 to 30 ft below the top of the Tipton in a 10-ft-thick layer correlating to the lower one-third of the retort chamber. The heads in the overlying 8-ft-thick sandstone layer are about 10 ft higher than those in the 10-ft-thick Tipton layer. This indicates a potential for flow to the 10-ft-thick Tipton layer from the overlying 8-ft-thick sandstone layer. Two sets of wells were used to examine heads in the horizontal direction. When the heads from all the wells completed in the 10-ft-thick Tipton layer are plotted, the values indicate a potential for horizontal flow to the southwest and west. A set of wells installed by Glover (1988), whose completion zones are open to the overlying 8-ft-thick sandstone layer and from one-third to nearly all of the Tipton, was used to compare head changes between 1982 and 1989. Because of variable completion intervals from well to well, the changes in head over the 7-year period were evaluated as to whether they were positive or negative. Heads have increased to the north of site 9 and decreased to the south.

CONCLUSION

The head values indicate a complex flow system at the White Mountain area in the vicinity of site 9. Temporal fluctuations indicate that the flow system is dynamic. Annual head changes as much as 10 ft are observed in the combination wells completed in both the overlying 8-ft-thick sandstone layer and larger intervals of the Tipton Shale Member of the Green River Formation and as much as 5 ft in wells completed in the overlying 8-ft-thick sandstone layer and the 10-ft-thick Tipton layer.

Spatial variability of head indicates a potential for vertical and horizontal flow. Paired wells indicate a potential for flow to the 10-ft-thick Tipton Shale Member layer from the overlying 8-ft-thick sandstone layer. Within the 10-ft-thick Tipton layer, there is potential for horizontal flow to the southwest and west. Head values from wells completed over a combined interval of the 8-ft-thick sandstone layer and Tipton indicate an increase of heads to the north of site 9 and a decrease to the south of site 9.

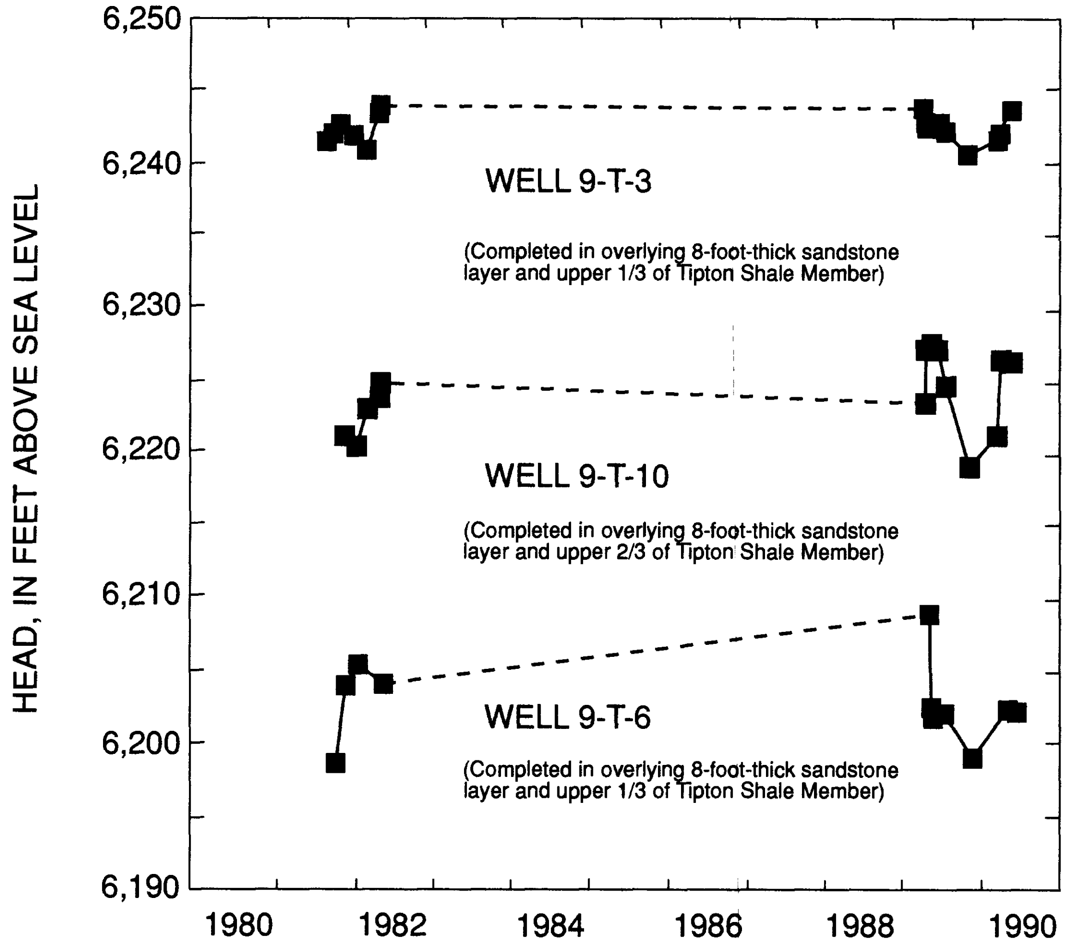

Figure 2. Head data for three wells, White Mountain *in-situ* oil-shale area, site 9.

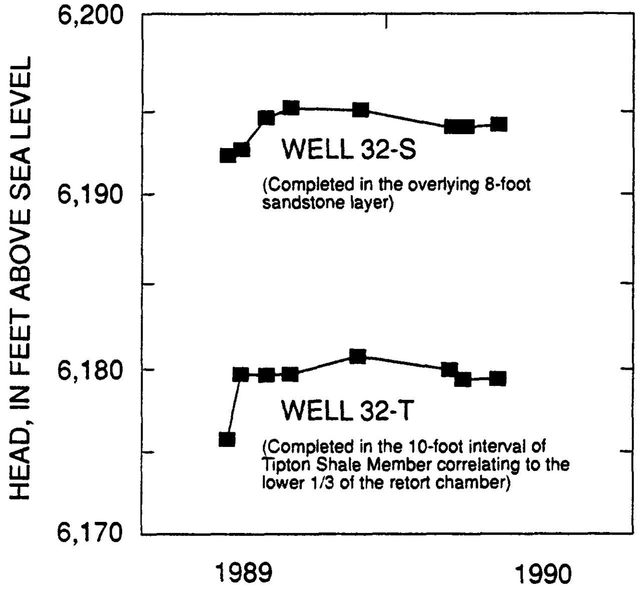

Figure 3. Head data for two paired wells, White Mountain *in-situ* oil-shale area, site 9.

The causes of the fluctuations in the head have not been determined. However, the head data indicate a dynamic system with a potential for both vertical and horizontal flow at the site.

REFERENCE

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USE OF AZAARENE TRACERS TO EVALUATE FRACTURE FLOW FROM AN *IN-SITU* OIL-SHALE RETORT, ROCK SPRINGS, WYOMING

By Larry B. Barber, II[1] *and* Jerry A. Leenheer[1]

ABSTRACT

Ground-water samples collected from an in-situ oil-shale retort site near Rock Springs, Wyoming, were analyzed for the presence of azaarene compounds (nitrogen heterocycles) to evaluate whether contaminants are moving offsite. Specific conductance, pH, and concentrations of dissolved organic and inorganic carbon also were measured. The composition of ground water collected from the retort chamber was very complex and more than 100 azaarene compounds were detected at concentrations ranging from 5 to greater than 1,000 micrograms per liter. None of the azaarenes present in the retort water were detected in downfield wells. Specific conductance, pH, and concentrations of dissolved organic and inorganic carbon were highly variable. Specific conductance ranged from 1,180 to 40,000 microsiemens per centimeters (at 25 degrees Celsius), pH ranged from 8.1 to 13.2, dissolved organic carbon ranged from 13 to 4,200 milligrams per liter, and dissolved inorganic carbon ranged from 5 to 4,600 milligrams per liter. Possible explanations for the absence of azaarenes in any wells other than the retort chamber include: (1) The contaminants have not been transported a measurable distance from the retort chamber because of very slow traveltimes; (2) the azaarenes are sorbed to the aquifer material; and (3) there is no direct hydrological connection through open fractures between the retort chamber and the wells studied.

INTRODUCTION

The physical properties of fracture flow are a continuum that ranges from large conduit flow in karst systems to microfractures in shales. In addition, most hydrologic systems are mixed, including zones of fracture flow and zones of porous flow. In mixed systems, it is difficult to distinguish which component is giving rise to the flow. One possible approach to distinguishing between porous and fracture flow is use of chemical tracers. Differences in the physicochemical properties of chemicals that control transport may be used to distinguish the type of flow regime on the basis of the following hypotheses: (1) Solutes transported through porous media undergo chromatographic separation as a function of the sorptive properties of the solid phase; and (2) solutes transported through open fractures have minimal contact with the aquifer solids and are not chromatographically separated.

The use of chemical tracers for distinguishing between porous and fracture flow in mixed systems was evaluated at an *in-situ* oil-shale retort site located near Rock Springs, Wyo. At this site, the sediments consist of low-permeability shale interspersed with permeable sandstone layers, providing the opportunity to evaluate the potential for using chemical tracers to distinguish between fracture and porous media flow.

Oil-shale retort water consists of hundreds of organic compounds including aliphatic and aromatic carboxylic acids, phenols, aromatic and aliphatic amines, hydroxypyridines, amides, nitriles, alcohols, ketones, and aldehydes (Leenheer and Noyes, 1986). The inorganic matrix also is very complex and contains high concentrations of sodium, bicarbonate, carbonate, chloride, various sulfur species, and ammonium. Retort waters typically have basic pH.

One particular class of organic compounds, azaarenes, was selected for this study. Azaarenes are aromatic nitrogen heterocycles, that are organic bases and can exist as neutral or ionic species, depending on the pH of the system. These compounds are formed by conversion of organic fuels (such as oil shale) into energy products, and are not common in the undisturbed natural environment. At the Rock Springs site, azaarenes are unique to the retort water and were formed at the time of retorting. In addition to being unique to the source, azaarenes have a wide range of physicochemical and sorptive properties; azaarene species range from highly soluble pyridine to low-solubility acridine. The extent and nature of sorption of azaarene compounds differs for the neutral and ionic species. The neutral species interact with the solid phase by partitioning into the sediment organic matter, whereas the protonated ionic species interact primarily by ion exchange (Zachara and others, 1987). Regardless of the ionization state, the sorption affinity increases with decreasing solubility. Neutral azaarene species predominate in the alkaline waters at the Rock Springs site.

This paper describes the results of a study in which ground-water samples were analyzed for azaarenes by XAD-8 adsorption chromatography combined with gas chromatography/mass spectrometry (GC/MS). The distribution of azaarene compounds was used to evaluate fracture- and porous-flow regimes in the aquifer.

METHODS

The location of the study site is shown in figure 1. Details on the history of the retort and on the geology and hydrology of the site can be found in Lidstone and Anderson, Inc. (1989) and Lindner-Lunsford and others (1990).

Ground-water samples were collected from 19 monitoring wells (fig. 1) by stainless steel bailer. One-liter ground-water samples were first spiked with surrogate standards, then vacuum filtered through a 1.0 micrometer glass-fiber filter, collected in amber glass bottles with Teflon[2]-lined caps, and stored at 4 °C (degrees Celsius) until analysis. Field measurements of pH and specific conductance were made on each sample.

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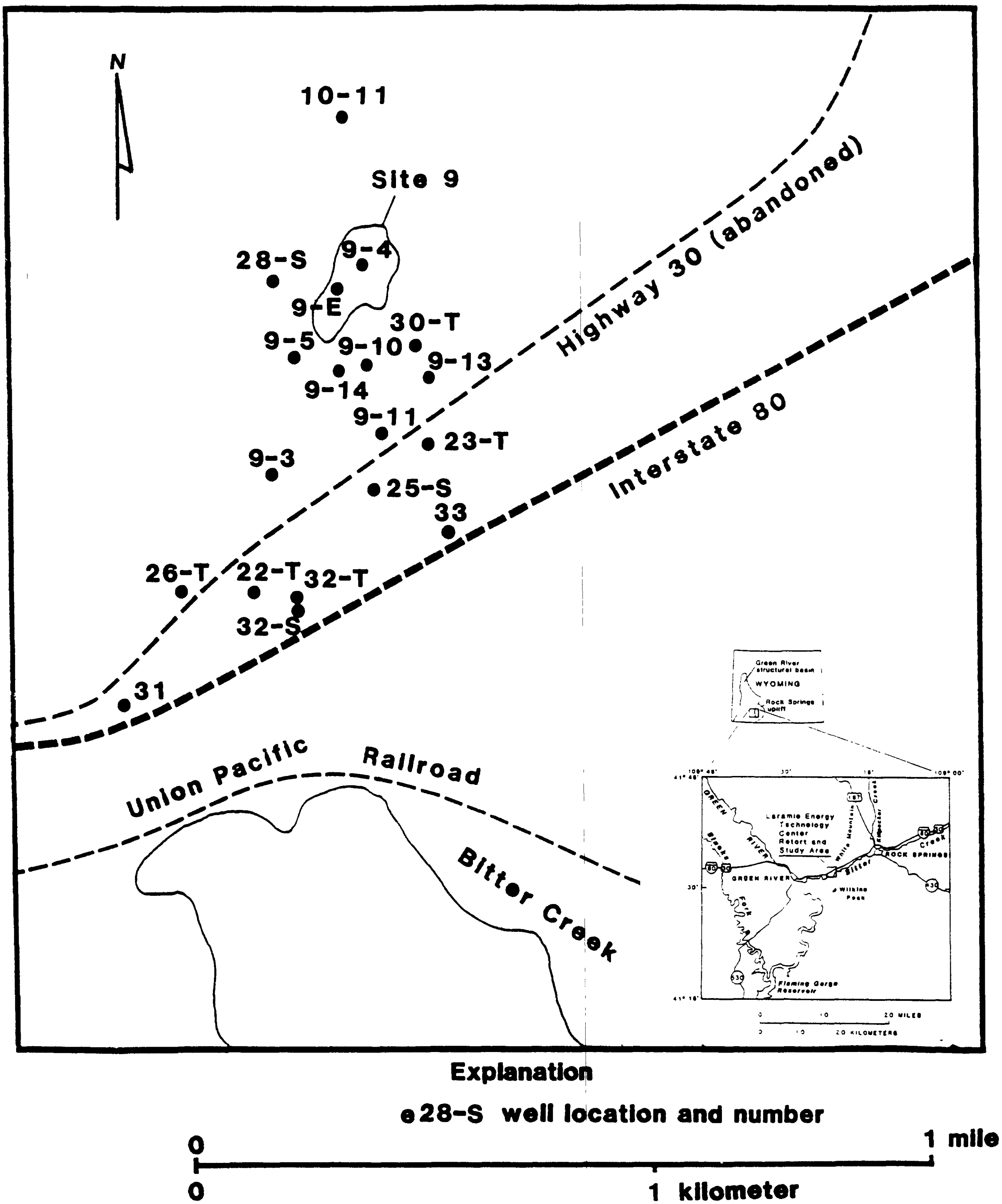
[1] U.S. Geological Survey, Lakewood, Colo.

[2] Use of brand, firm, or trade names in this paper is for identification purposes only and does not imply endorsement by the U.S. Geological Survey.



N
10-11
Site 9
28-S
9-4
9-E
30-T
9-5
9-10
9-13
9-14
9-11
23-T
9-3
25-S
33
26-T
22-T
32-T
32-S
31
Highway 30 (abandoned)
Interstate 80
Union Pacific Railroad
Bitter Creek
Green River structural basin
WYOMING
Rock Springs uplift
109° 45'
30'
15'
109° 00'
41° 45'
30'
41° 15'
GREEN RIVER
Blacks Fork
Laramie Energy Technology Center Retort and Study Area
White Mountain
Killpecker Creek
187
80
30
Bitter Creek
ROCK SPRINGS
GREEN RIVER
Wilkins Peak
430
530
Flaming Gorge Reservoir
0 10 20 MILES
0 10 20 KILOMETERS
Explanation
● 28-S well location and number
0
1 mile
0
1 kilometer

Figure 1. Location map showing study site and wells discussed in this report.

Deuterated azaarene surrogate standards (d_5-pyridine, d_7-quinoline, and d_9-acridine) were added to samples at the time of collection to: (1) Evaluate the analytical procedure; (2) monitor loss of sample components due to sorption and biodegradation; and (3) provide precise quantitative data. The nondeuterated analogs of these compounds cover a broad range of physicochemical properties and were present in the retort water.

Azaarenes were isolated by the method of Stuber and Leenheer (1982). This method involves concentration from water on columns of adsorbent resin and recovery by aqueous-acid elution. A 20-mL (milliliter) column was packed with XAD-8 resin. Prior to sample concentration, the resin was conditioned by passing 25 mL of 0.1 N (normal) sodium hydroxide (NaOH), 30 mL of 0.1 N hydrochloric acid (HCl), 50 mL of 80:20 (by volume) acetonitrile:HCl, and 100 mL of distilled water through the column. Next, 200 mL of sample was passed through the column (flow rate=4 mL per minute) followed by 25 mL of distilled water. The column was inverted and back eluted with 100 mL of 0.1 N HCl and pumped to dryness. The eluant was rotary evaporated to dryness (40 °C, 790 torr), and the azaarene hydrochlorides were converted to the free amines by redissolving the residue in 0.5 mL of distilled water and adding 0.1 mL of saturated NaOH. The amines were extracted into methylene chloride, and perdeuteronaphthalene was added as an internal standard. The methylene chloride extracts were analyzed by GC/MS. Mass-spectra data were collected in the full-scan and selected-ion-monitoring (SIM) modes. Concentrations of individual azaarenes were calculated from the SIM data using response factors from analysis of standards. Samples also were analyzed for concentrations of dissolved nonpurgeable organic carbon (DOC), dissolved purgeable organic carbon (POC), and dissolved inorganic carbon (DIC).

RESULTS

Distilled-water spike-and-recovery experiments were conducted using 18 azaarene standards (pyridine, d_5-pyridine, 10 alkyl pyridines, quinoline, d_7-quinoline, 2 alkyl quinolines, acridine, and d_9-acridine) spiked at 50 µg/L (micrograms per liter). Compound recoveries ranged from 10 percent to greater than 100 percent, with a mean recovery (n=3) of 85 percent. Recoveries greater than 100 percent are an artifact of the quantitation method. Recovery was highest for alkyl pyridines, quinoline, and alkyl quinolines, and lowest for acridine and pyridine. Mean recovery (n=20) for deuterated surrogate standards spiked into the ground-water samples was 50 percent for d_5-pyridine, 65 percent for d_7-quinoline, and 35 percent for d_9-acridine. The low recovery of d_5-pyridine may be caused by poor adsorption efficiency and loss during eluant volume reduction as a result of azeotropic coevaporation with methylene chloride. The low recovery of d_9-acridine is likely caused by incomplete elution from the resin and sorption to glassware. The approximate detection limit for the method is 5 µg/L.

Determination of individual compounds in a complex matrix, such as the ground water at the study site, is difficult because of high concentrations of dissolved organic and inorganic compounds, the presence of particulate matter, and, in some cases, the presence of an oil phase. The azaarene composition of ground water from the retort chamber (well 9-4) was extremely complex; more than 150 azaarene compounds were found at concentrations greater than 5 µg/L. Most of the compounds were alkyl (C_1-C_8) pyridine and alkyl (C_1-C_5) quinoline isomers. Tables 1 and 2 summarize concentration data for the retort water for target azaarenes for which standards are available, and for nontarget azaarenes listed according to the alkyl homolog. Analysis of samples downfield from the retort chamber did not detect any azaarene compounds at concentrations of 5 µg/L or greater.

Table 3 summarizes data on pH, specific conductance, and concentrations of DOC, POC, and DIC. These data are plotted in figure 2. Values for pH ranged from 8.1 to 13.2 and did not show any trend with respect to the direction of ground-water flow, or indicate transport through open fractures. Specific conductance ranged from 1,180 to 40,000 microsiemens per centimeter (at 25 °C) and, as with pH, did not show any spatial trends. The pH and specific-conductance data did not correlate with each other or with other constituents. Total dissolved organic carbon (DOC+POC) concentrations ranged from 13 to 4,200 mg/L (milligrams per liter); POC comprised 1 to 20 percent of the total organic carbon. DIC ranged from 5 to 4,600 mg/L, and DOC:DIC ratios were 0.04 to 9.41. As was the case for pH and specific conductance, DOC, POC, and DIC distributions showed no spatial trends.

DISCUSSION

Under pH conditions of ground water at the Rock Springs site (pH >8.0) pyridine, quinoline, and acridine are in their unprotonated neutral form, and sorption processes are controlled by partitioning into the sediment organic matter (Zachara and others, 1987). The approximate rate of transport can be predicted from the octanol-water partition coefficient (K_{ow}) and the fractional sediment organic carbon content (f_{oc}) by the following empirical equation (Schwarzenbach and others, 1983):

$$R_f = \frac{V_w}{V_s} = 1 + 3.2\ (f * f_{oc} * K_{ow}{}^{0.72})\ \frac{\rho(1-\varepsilon)}{\varepsilon}$$

where R_f is the relative retardation factor, V_w is ground water flow velocity (centimeters per second), V_s is solute flow velocity (centimeters per second), f is fraction of sediment responsible for sorption, ρ is grain density of solid phase (grams per cubic centimeters), and ε is porosity.

For our discussions here, we consider f to be the difference between porous flow (large fraction of bulk aquifer material available for reaction) and fracture flow (small fraction of bulk aquifer material available for sorption). Table 4 summarizes predicted R_f values based on f= 0.5 for porous flow and f= 0.1 for fracture flow, and f_{oc}= 0.01, 0.10, and 0.30. These f_{oc} values are estimated to represent the range of sediment organic carbon values that might be encountered at the Rock Springs site. The density was assumed to be 2.6 grams per cubic centimeter, and two values of porosity were used (ε= 0.35 for sandstone and ε= 0.1 for shale). As can be seen from table 4, if transport is through a zone of high-f_{oc} porous media (f_{oc}=0.1, porosity = 0.35), using an estimated flow velocity of 100 ft/yr (feet per year),

Table 1. *Summary of concentration data for azaarene target compounds and surrogate standards in retort water analyzed gas chromatography/mass spectrometry in full scan mode*

[RT=retention time; μg/L=microgram per liter; SS=surrogate standard; IS=internal standard; nd=not detected]

Compound	RT	Concentration (μg/L)
d_5-pyridine (SS)	4.79	17
Pyridine	4.79	490
2-methylpyridine	7.30	3
3-,4-methylpyridine[1]	8.95	140
2,6-dimethylpyridine	9.99	120
2-ethylpyridine	10.92	20
2,4-dimethylpyridine	11.97	690
4-ethylpyridine	13.64	6
3,5-dimethylpyridine	14.28	21
2,4,6-trimethylpyridine	14.89	750
3,4-dimethylpyridine	15.13	120
2,3,6-trimethylpyridine	15.45	190
d_8-napthalene (IS)	22.46	50
d_7-quinoline (SS)	24.53	50
Quinoline	24.66	nd
Methylquinoline	27.27	280
Acridine	41.20	nd
d_9-acridine (SS)	42.20	15

[1] Compounds coelute

Table 2. *Summary of data for nontarget alkylpyridine and alkylquinoline isomers, and total azaarenes in retort water. Compounds grouped according to increasing number of alkyl substituents (C_n)*

[Concentrations in micrograms per liter (μg/L)]

Compound	Number of isomers	Total concentration (μg/L)
C_1-pyridine	5	310
C_2-pyridine	12	1,330
C_3-pyridine	10	1,570
C_4-pyridine	18	3,190
C_5-pyridine	27	2,030
C_6-pyridine	20	720
C_7-pyridine	9	280
C_8-pyridine	1	35
C_1-quinoline	2	400
C_2-quinoline	8	990
C_3-quinoline	21	510
C_4-quinoline	6	160
C_5-quinoline	2	13
Total azaarenes	141	11,600

even the most mobile compound (pyridine) would be transported only 20 ft (feet) in 1 year or 260 ft in the 13 years since retorting of the oil shale. If flow is through open fractures, the relative transport velocity for pyridine (assuming the same conditions) would be approximately 50 ft/yr or 650 ft distance in 13 years. Even though it is unlikely that ground-water flow through unfractured shale is more than a few feet per year, these calculations show that relative velocities of fracture flow should be significantly greater than those of porous flow. In porous media, sorption of azaarene compounds would result in significant removal from solution.

Based on the above calculations, the absence of azaarenes at concentrations above the method detection limit (approximately 5 μg/L) in wells other than the retort chamber may result from the following conditions: (1) Flow velocities are so low that contaminated ground water has not migrated the distance of the downgradient wells; (2) the wells are not in direct hydrological connection through open fractures with the retort chamber; and (3) azaarenes have been removed from ground water by sorption to the aquifer sediments. Because of the finely laminated structure of oil shale, it is possible that flow is through microbedding planes, and, although flow is through fracture-type apertures, the net flow cannot be differentiated from porous-media flow. On the basis of these preliminary data, ground water has not been transported by open-fracture flow from the retort chamber to the wells sampled in this study.

Although the effect of biodegradation was not considered in this study, compounds such as quinoline can be readily transformed by appropriate microorganisms (Pereira and others, 1988). Although biological degradation cannot be ruled out as having an effect on the transport of azaarene compounds at the site, it is unlikely that the complete absence of azaarene compounds detected in the retort water in any of the other wells is caused by biodegradation. Also, no azaarene metabolites were detected in any of the wells.

The lack of spatial relations between pH, specific conductance, and concentrations of DOC, POC, and DIC is likely the result of: (1) Natural variability in the ground-water geochemistry because of geological controls; (2) vapor-phase transport through unsaturated microfractures at the time of retorting; and (3) post-retorting transport of nonazaarene constituents.

SUMMARY

Ground-water samples from an *in-situ* oil-shale retort site were analyzed for azaarene compounds by adsorption chromatography using GC/MS for compound detection and identification. Water from the retort chamber contained high concentrations of a complex suite of alkyl pyridine and alkyl quinoline compounds. However, none of the azaarene compounds identified in the retort water were detected in any other wells, indicating that the contaminated ground water is not being transported at rates high enough to be detected in the downgradient wells.

Table 3. *Summary of pH, specific conductance, dissolved nonpurgeable organic carbon, dissolved purgeable organic carbon, total dissolved organic carbon, dissolved inorganic carbon, and total azaarenes*

[Sp. cond., Specific conductance; DOC, dissolved nonpurgeable organic carbon; POC, dissolved purgeable organic carbon; TOC, total dissolved organic carbon; DIC, dissolved inorganic carbon; Aza, azaarenes; (μS/cm)=microsiemens per centimeter; mg/L=milligrams per liter; nd, not detected]

Well No.	pH	Sp cond μS/cm	DOC mg/L	POC mg/L	TOC mg/L	POC/ TOC	DIC mg/L	DIC/ TOC	Total Aza mg/L
10-11	9.7	8,600	80	4	84	0.05	590	7.0	nd
9-4	9.5	30,000	470	90	560	.16	2,700	4.8	15
9-E	--	--	66	1	67	.02	210	3.1	nd
28-S	--	--	3,800	230	4,030	.06	690	.2	nd
9-5	9.2	21,000	22	2	24	.06	160	6.8	nd
30-T	12.9	28,000	130	1	131	.01	5	.0	nd
9-10	9.9	30,000	150	7	157	.04	1,020	6.5	nd
9-14	9.6	1,180	12	1	13	.09	75	5.7	nd
9-13	9.3	14,000	960	50	1,010	.05	620	0.6	nd
9-11	8.9	13,500	85	5	90	.06	450	5.0	nd
23-T	13.0	28,000	60	5	65	.08	11	.2	nd
9-3	9.0	20,000	320	78	398	.20	390	1.0	nd
25-S	10.0	40,000	4,080	120	4,200	.03	4,600	1.1	nd
33	8.3	16,000	44	3	47	.06	240	5.1	nd
26-T	8.5	6,500	33	2	35	.05	202	5.8	nd
22-T	13.2	4,800	85	8	93	.08	120	1.3	nd
32-T	8.1	20,000	61	5	66	.07	620	9.4	nd
32-S	10.1	38,000	3,900	95	3,995	.02	3,800	1.0	nd
31	9.5	11,000	58	8	66	.12	330	5.0	nd

Table 4. *Summary of relative retardation factors (Rf) for pyridine, quinoline, and acridine based on partitioning into sediment organic carbon*

[Data calculated from the equation of Schwarzenbach and Westall, 1983, below]

	Rf for f=0.5						Rf for f=0.1					
	f_{oc} 0.3		f_{oc} 0.1		f_{oc} 0.01		f_{oc} 0.3		f_{oc} 0.1		f_{oc} 0.01	
	Porosity		Porosity		Porosity		Porosity		Porosity		Porosity	
Compound	35%	10%	35%	10%	35%	10%	35%	10%	35%	10%	35%	10%
Pyridine	13	60	5	21	1	3	3	13	2	5	1	1
Quinoline	69	332	24	111	3	12	15	67	6	23	2	3
Acridine	650	3150	218	1050	23	815	131	632	44	211	5	23

$$R_f = 1 + 3.2\, f\, f_{oc}\, K_{ow}^{0.72}\, \frac{\rho(1-\varepsilon)}{\varepsilon} = \frac{V_w}{V_s}$$

K_{ow} pyridine = 10.
K_{ow} quinoline = 110.
K_{ow} acridine = 2512.
K_{ow} values from Zachara and others, 1987.
f= fraction of total sediment mass involved in sorption.
f_{oc}= fractional sediment organic carbon content.
K_{ow}= octanol/water partition coefficient.
ρ= bulk density of the sediment = 2.6 grams per cubic centimeter
ε= porosity

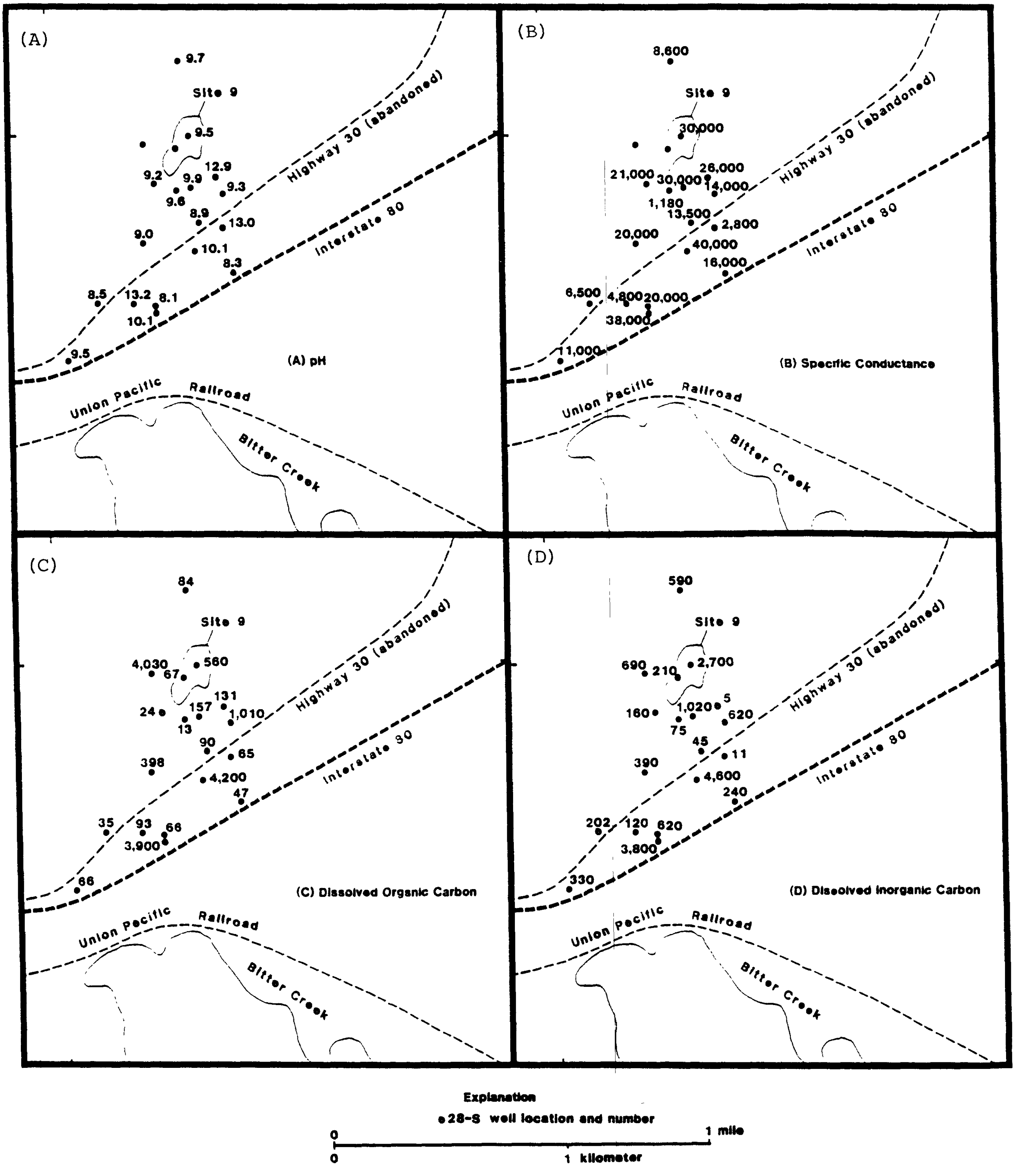

(A)
• 9.7
Site 9
• 9.5
12.9
9.2
9.9
9.3
9.6
8.9
13.0
9.0
10.1
8.3
8.5
13.2
8.1
10.1
9.5
Highway 30 (abandoned)
Interstate 80
(A) pH
Union Pacific Railroad
Bitter Creek
(B)
8,600
Site 9
30,000
26,000
21,000
30,000
14,000
1,180
13,500
2,800
20,000
40,000
16,000
6,500
4,800
20,000
38,000
11,000
Highway 30 (abandoned)
Interstate 80
(B) Specific Conductance
Union Pacific Railroad
Bitter Creek
(C)
84
Site 9
4,030
560
67
131
24
157
1,010
13
90
65
398
4,200
47
35
93
66
3,900
66
Highway 30 (abandoned)
Interstate 80
(C) Dissolved Organic Carbon
Union Pacific Railroad
Bitter Creek
(D)
590
Site 9
690
210
2,700
5
160
1,020
620
75
45
11
390
4,600
240
202
120
620
3,800
330
Highway 30 (abandoned)
Interstate 80
(D) Dissolved Inorganic Carbon
Union Pacific Railroad
Bitter Creek
Explanation
• 28-S well location and number
0
1 mile
0
1 kilometer

Figure 2. Distribution patterns for (A) pH, (B) specific conductance (microsiemens per centimeter at 25 degrees Celsius), (C) concentrations of dissolved organic carbon (milligrams per liter), and (D) concentrations of dissolved inorganic carbon (milligrams per liter).

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GEOGRAPHIC AND TEMPORAL DISTRIBUTION OF HERBICIDES IN SURFACE WATERS OF THE UPPER MIDWESTERN UNITED STATES, 1989-90

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ABSTRACT

Results from a 2-year study of 149 streams geographically distributed across the corn-producing region of 10 Midwestern States show that detectable concentrations of herbicides persist year round in most streams. During late spring and summer, concentrations of one or more herbicides exceeded U.S. Environmental Protection Agency proposed maximum contaminant levels for drinking water in more than one-half the streams sampled. Some herbicides exceeded proposed maximum contaminant levels during runoff for periods of several weeks to several months. Atrazine was the most frequently detected and most persistent herbicide measured, followed by desethylatrazine (an atrazine metabolite) and metolachlor. Alachlor and cyanazine were detected primarily during the late spring and summer. The seasonal distribution of atrazine indicates that aquifers contributing base flow to the streams are contaminated with herbicides. Results from this study, which are believed to be applicable to other streams throughout the upper Midwest, indicate an annual cycle of herbicide application, a series of flushing events during which herbicides are transported into streams and ground water, and periods of base flow during which persistent herbicides are discharged into the streams from ground-water sources.

INTRODUCTION

Large quantities of agricultural chemicals are used each year in the upper Midwestern United States (fig. 1) in the production of corn, soybeans, and other agricultural products. This region produces more than 75 percent of the corn and more than 60 percent of the soybeans grown in the country (U.S. Department of Agriculture, 1985). In producing these agricultural products, large quantities of

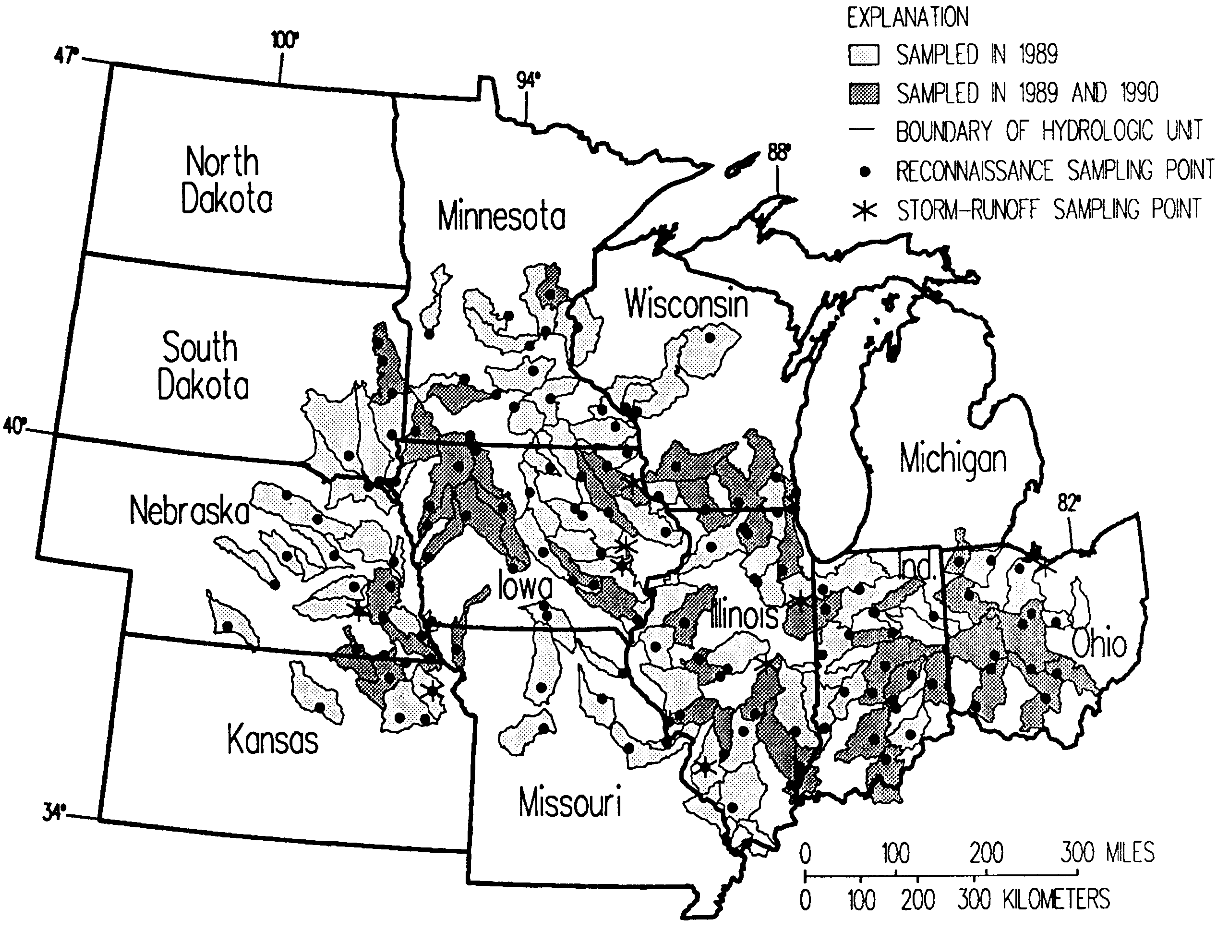
EXPLANATION
☐ SAMPLED IN 1989
▨ SAMPLED IN 1989 AND 1990
— BOUNDARY OF HYDROLOGIC UNIT
● RECONNAISSANCE SAMPLING POINT
✳ STORM-RUNOFF SAMPLING POINT
47°
100°
94°
88°
82°
40°
34°
North Dakota
Minnesota
South Dakota
Wisconsin
Michigan
Nebraska
Iowa
Illinois
Ind.
Ohio
Kansas
Missouri
0 100 200 300 MILES
0 100 200 300 KILOMETERS

Figure 1. Map of the upper Midwestern United States showing location of study area, hydrologic units, and sites sampled in 1989 and 1990.

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[1] U.S. Geological Survey, Denver, Colo.
[2] U.S. Geological Survey, Lawrence, Kans.
[3] U.S. Geological Survey, Iowa City, Iowa

pesticides, primarily herbicides, are applied to cropland. In 1982, about 224 million pounds of pesticides (active ingredients thereof) were used in the 10 States that form this region (fig. 1, table 1; Gianessi and Puffer, 1988). The herbicides alachlor, atrazine, cyanazine, and metolachlor account for about 73 percent of the pesticides used.

Table 1. *Quantities of major herbicides used in 10 Midwestern States*

[From Gianessi and Puffer, 1988; values shown are in millions of pounds of active ingredient per year]

State	Alachlor	Atrazine	Metolachlor	Cyanazine
Illinois	11.2	10.8	8.9	3.4
Indiana	7.1	8.2	3.0	1.3
Iowa	11.4	7.4	9.6	9.4
Kansas	3.0	5.2	.2	.1
Minnesota	9.1	3.1	1.4	2.3
Missouri	4.1	3.4	2.5	.5
Nebraska	5.0	6.9	.5	1.2
Ohio	6.5	4.9	4.4	1.5
South Dakota	2.7	1.0	.3	.4
Wisconsin	3.3	5.8	1.4	1.0

The intense use of herbicides in conjunction with their moderately large solubility and mobility poses potentially serious problems for nonpoint-source contamination of ground- and surface-water resources in the Midwest. Numerous studies concerning ground-water contamination by herbicides have been conducted in the last several years. Much of this work was summarized by Hallberg (1989). However, except for recent studies by Squillace and Engberg (1988), and Pereira and others (1989), and very little has been done to address contamination of surface waters by agricultural chemicals at regional and multi-State scales. The U.S. Geological Survey (USGS) through its Toxic Substances Hydrology Program began a series of regional studies in the Midwest in 1989 to address this area of concern. The overall objective of the regional studies is to determine the occurrence and distribution of commonly used herbicides and their metabolites in streams of the upper Midwest. Two specific objectives are to (1) determine the geographic and seasonal distribution of commonly used herbicides in streams of different size over a 10-State area, and (2) determine the temporal distribution in concentrations and loads of 11 herbicides and 2 metabolites in selected midwestern streams during periods of storm runoff.

This paper describes some early results of a regional reconnaissance for herbicides in surface water that was conducted during 1989 and 1990, and of a study of herbicide transport during storm runoff in the late spring and summer of 1990.

STUDY DESIGN

Sampling sites were selected at 149 locations on streams in a 10-State area comprising the corn belt (fig. 1). These States include Illinois, Indiana, Iowa, Kansas, Minnesota, Missouri, Nebraska, Ohio, South Dakota, and Wisconsin. The sampling sites were selected at USGS streamflow-gaging stations by a stratified random procedure designed to ensure geographic distribution. The drainage area of the hydrologic units in which the sampling sites were located ranged from 89 to more than 10,000 mi^2 (square miles). The median drainage area was 770 mi^2. Most of the sites were sampled three times in 1989--(1) before application of herbicides (March-April); (2) after application and during the first runoff event (May-June); and (3) in the fall during a low-flow period (October-November), when most of the streamflow was derived from ground water.

One-third of the sites were resampled during 1990 before and after herbicide application. The sampling locations were selected by a stratified random process that took into account results of postapplication analyses of the 1989 samples. The sites sampled in 1989 were ranked from largest to smallest total herbicide concentrations; 50 percent of the sites 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 ranked concentration.

All water samples were collected by depth-integrating techniques from three to five locations across each stream. The samples were collected and composited in large glass containers, filtered through glass-fiber filters (1-micrometer pore diameter) into heat-cleaned glass bottles for shipment to the laboratory. Field measurements of specific conductance, pH, and temperature were made on all samples.

Most samples collected in 1989 were analyzed for triazine herbicides by an enzyme-linked immunosorbent assay procedure (ELISA) (Goolsby and others, 1990). In addition, about one-third of the preapplication samples and all of the postapplication and fall low-flow samples were analyzed for 11 herbicides and 2 metabolites (table 2) by gas chromatography/mass spectrometry (GC/MS) using

Table 2. *Herbicides analyzed and percent detections in preapplication, postapplication, and fall low flow samples during 1989 and 1990*

[μg/L, micrograms per liter; N, number of samples analyzed; <, less than. 1990 samples are from a stratified random subset of sites sampled in 1989 and are biased toward a slightly higher detection rate]

Herbicide	Reporting limit (μg/l)	Percentage detections greater than reporting limit				
		1989 pre-application (N=55)	1989 post-application (N=132)	1989 fall low-flow (N=145)	1990 pre-application (N=52)	1990 post-application (N=45)
Alachlor	.05	18	86	12	50	100
Ametryn	.05	0	0	0	0	0
Atrazine	.05	91	98	76	96	100
Cyanazine	.20	5	63	0	8	89
Desethylatrazine	.05	54	86	47	86	98
Desisopropylatrazine	.05	9	54	0	44	96
Metolachlor	.05	34	83	44	67	100
Metribuzin	.05	2	53	0	0	62
Prometon	.05	0	23	6	10	20
Prometryn	.05	0	0	0	0	0
Propazine	.05	0	40	<1	0	71
Simazine	.05	7	55	3	15	64
Terbutryn	.05	0	0	0	0	0

procedures described by Thurman and others (1990). All of the samples collected in 1990 were analyzed for herbicides by GC/MS.

Automatic samplers on nine streams in Illinois, Iowa, Kansas, Nebraska, and Ohio (fig. 1) were used to determine the temporal distribution of herbicides during storm runoff in the spring and summer of 1990. The drainage areas sampled ranged from 100 to more than 5,000 mi^2. Samples were collected several times per week during base-flow periods and every few hours during storm runoff events. All samples were analyzed for specific conductance, pH, nitrite plus nitrate, and triazine herbicides by ELISA. About 25 percent of the samples were selected for herbicide analysis by GC/MS methods.

RESULTS AND DISCUSSION

The herbicides detected most frequently and in largest concentrations were atrazine, alachlor, cyanazine, and metolachlor (table 2, fig. 2.). These herbicides are among the most heavily used in the region (table 1). Herbicides were detected most frequently during the postapplication period when concentrations of atrazine were detected at 98 percent of the sites. Alachlor, metolachlor, and desethylatrazine, (an atrazine metabolite) were detected at more than 80 percent of the sites and cyanazine was detected at more than 60 percent of the sites during the 1989 postapplication sampling period.

Herbicide concentrations during the postapplication period were generally one to two orders of magnitude larger than those measured before application and in the fall during low streamflow (fig. 2). For example, the median concentration of atrazine during the postapplication period was 3.8 µg/L (micrograms per liter) compared with about 0.2 µg/L during the preapplication and fall low-flow periods. Similar seasonal distributions were observed for the other major herbicides (fig. 2.). The total herbicide concentration, defined here as the sum of the concentrations of the 11 herbicides and 2 metabolites determined by GC/MS, was calculated for each sample. The results (fig. 2) show that the median total herbicide concentration in the 1989 postapplication samples was 8.7 mg/L, or more than 20 times larger than the preapplication and fall low-flow concentrations.

The distributions in herbicide concentrations for approximately 50 sites randomly selected for resampling in 1990 were almost identical to those determined for 1989 samples. Figure 3 shows the preapplication and postapplication concentration distributions for several herbicides sampled in both years. Only data from the 50 randomly selected sites were used for this figure. The results indicate that herbicides in large concentrations are flushed from cropland each year and move through the surface-water system as pulses in response to late-spring and early-summer rainfall. This pulse effect appears to occur over a large area of the Midwest and is linked to agricultural land-use patterns and climate.

Postapplication concentrations of four major herbicides exceeded U.S. Environmental Protection Agency proposed maximum contaminant levels (PMCL) or lifetime health advisories (HA) for drinking water (U.S. Environmental Protection Agency, 1988; Federal Register, 1989; 1990) for a short but undetermined period of time in both 1989 and 1990 (table 3). For example, the atrazine concentration exceeded the PMCL of 3 µg/L in more than 50 percent of the samples in both years and the alachlor concentration exceeded the PMCL of 2 µg/L in more than 30 percent of the samples in both years. A small percentage of samples also exceeded PMCL or HA for simazine and cyanazine. In contrast, only the concentration of atrazine in three preapplication samples (one in 1989 and two in 1990) and one fall low-flow sample exceeded the PMCL or HA. It should be noted that the PMCL and HA do not consider the cumulative or synergistic effects that might result if more than one herbicide exceeds these levels. In the 1989 post-application period, for example, samples from 23 percent of the sites exceeded PMCL or HA for two herbicides and 10 percent exceeded PMCL or HA for three herbicides.

Table 3. *Comparison of post-application herbicide concentrations with proposed maximum contaminant levels and health advisory levels for drinking water*

[HA, health advisory; PMCL, U.S. Environmental Protection Agency proposed maximum contaminant level; µg/L, micrograms per liter; N, number of samples analyzed; --, no data; (a), PMCL used for comparison. 1990 samples are from a stratified random subset of sites sampled in 1989 and are biased toward slightly higher concentrations]

Herbicide	Lifetime HA (µg/L)	PMCL (µg/L)	Percent of samples in which concentration exceeded HA or PMCL	
			1989 (N=132)	1990 (N=45)
Alachlor	--	2	32	42
Atrazine	3	3	52	71
Cyanazine	10	--	11	16
Metolachlor	100	--	0	0
Metribuzin	200	--	0	0
Propazine	10	--	0	0
Prometron	100	--	0	0
Simazine (a)	4	1	7	13

Preliminary results from analyses of samples collected with automatic samplers in the spring and summer of 1990 indicate that herbicide concentrations persist above PMCLs during periods of storm runoff for several weeks to several months following herbicide application to cropland. For example, figure 4 shows a hydrograph of streamflow and a time-series plot of triazine concentrations obtained from ELISA analysis of samples from the Iroquois River near Chebanse, Ill., which drains an area of 2,091 mi^2. These results indicate that the atrazine concentration exceeded the 3 µg/L PMCL during much of May, and parts of June and July. Storm runoff samples collected in a similar manner at sites in Iowa, Kansas, Nebraska, Ohio, and other sites in Illinois show a similar pattern of triazine concentrations on the basis of ELISA.

The information obtained to date indicates that atrazine is the most persistent of the major herbicides in surface waters of the Midwest, followed in order of decreasing persistence by desethylatrazine, metolachlor, alachlor, and cyanazine. This conclusion is based primarily on the detection frequencies shown in table 2. Atrazine was detected year round in most of the streams sampled, and desethylatrazine was detected year round at about half the sites. Alachlor and cyanazine, on the other hand, were detected primarily following application.

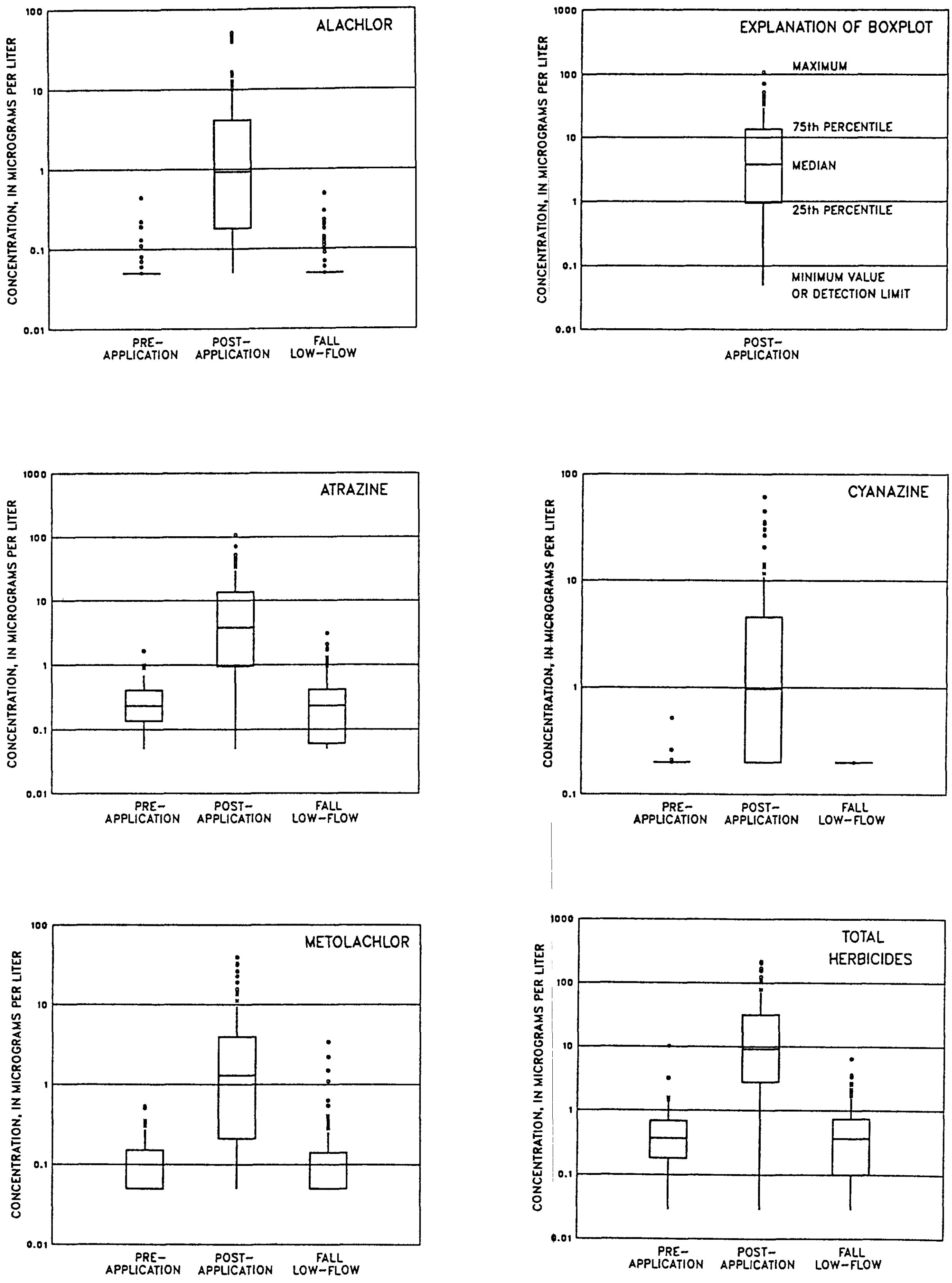

Figure 2. Boxplots showing the seasonal distribution in concentrations of selected herbicides detected during three sampling periods in 1989.

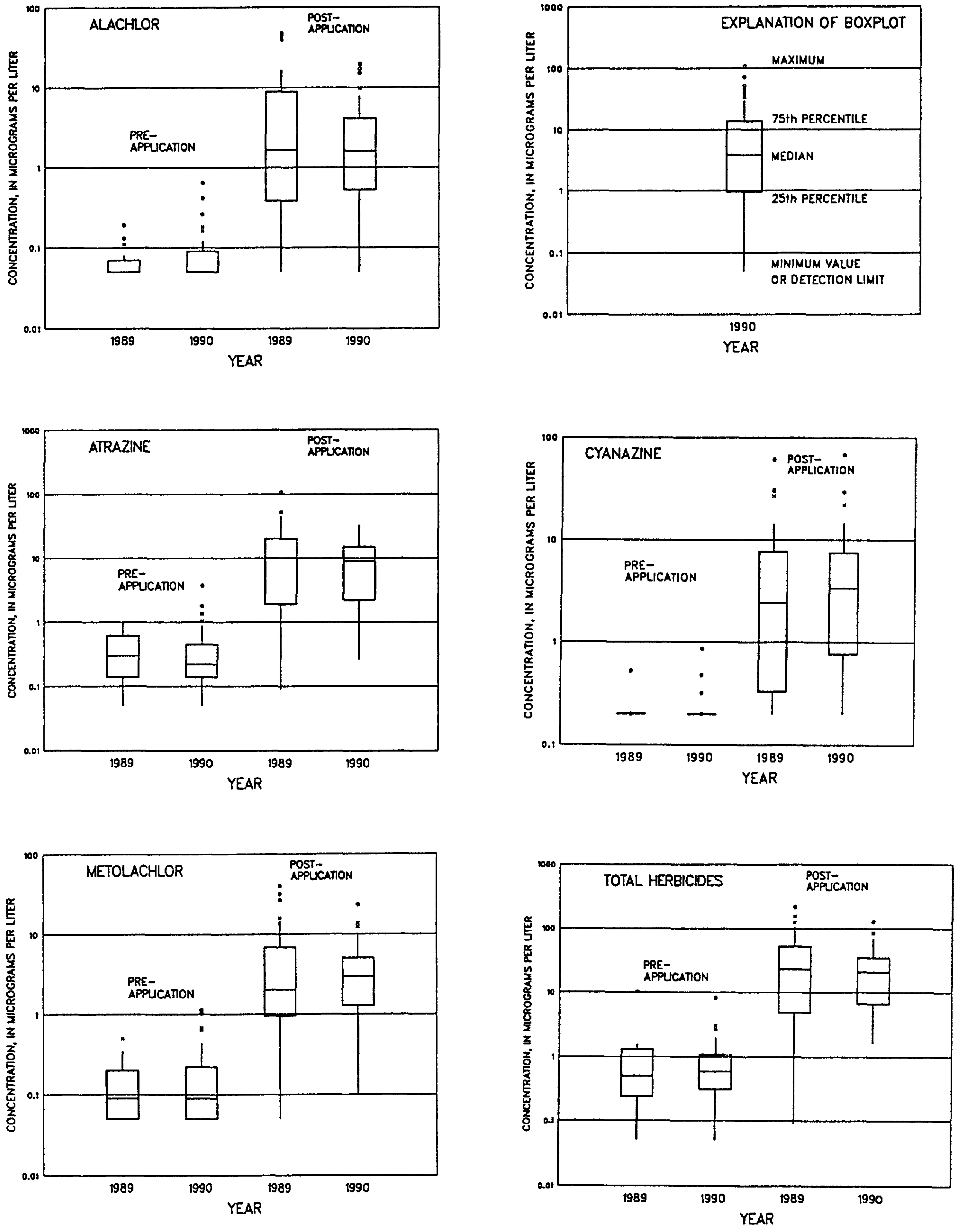

Figure 3. Boxplots showing the distribtions in concentrations of selected herbicides at approximately 50 sites sampled both in 1989 and 1990 during pre- and postapplication sampling periods.

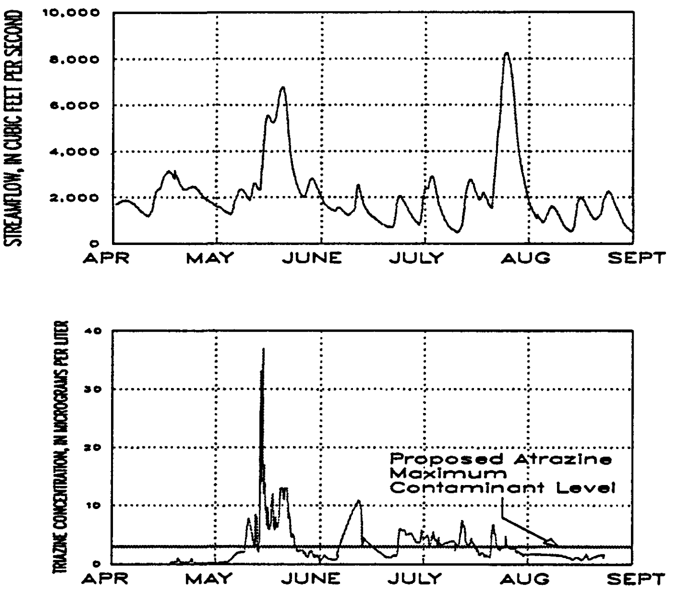

Figure 4. Hydrographs showing streamflow and triazine concentrations from ELISA analysis for the Iroquois River near Chebanse, Illinois, mid-April to late July 1990.

The high frequency of detection of atrazine, desethylatrazine, and metolachlor in the fall when the streamflow was derived primarily from ground-water inflow (base flow) indicates that aquifers contributing base flow to the streams are contaminated, to variable extent, with herbicides. Contamination of these aquifers may occur during postapplication flushing events when the streams and recharge water contain very large concentrations of herbicides. The process by which ground water becomes contaminated is complex and may include recharge resulting from overbank flooding, recharge by contaminated upland runoff, and bank storage, among other causes. The contaminated ground water can discharge to the river during periods of base flow and, thus, may represent a persistent source of herbicides to the streams.

SUMMARY

Detectable concentrations of herbicides persist year round in most streams in the corn-producing region of the upper Midwest. Herbicide concentrations measured in 1989 during late spring and summer runoff after application were one to two orders of magnitude larger than those measured both before application and during low streamflow in the fall. Of the 13 herbicides and metabolites measured, atrazine, alachlor, metolachlor, and cyanazine were present in the largest concentrations. During late spring and summer, concentrations of one or more herbicides exceeded PMCL for drinking water 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 exceed PMCL during runoff for periods of several weeks to several months after application. Atrazine was the most frequently detected and most persistent herbicide measured, followed by desethylatrazine 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 with 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 periods of base flow during which persistent herbicides in ground water slowly reenter into the streams. Results from this study are believed to be applicable to most streams throughout the upper Midwest.

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SOURCE OF ATRAZINE, DESETHYLATRAZINE, METOLACHLOR IN A SELECTED REACH OF THE CEDAR RIVER, IOWA, DURING BASE-FLOW CONDITIONS

By Paul J. Squillace[1], E.M. Thurman[2], Edward E. Fischer[1], *and* Phil J. Soenksen[1]

ABSTRACT

A budget of atrazine, desethylatrazine, and metolachlor loads was computed for a 116-kilometer reach of the Cedar River in Iowa to determine where these compounds enter the river during base-flow conditions. Loads were determined by measuring discharge and concentrations of the compounds for four main-stem sites along the Cedar River and for 27 tributaries on September 20-22, 1989. Tributaries contributed 17 percent of the increased atrazine load, 24 percent of the increased desethylatrazine load, and 38 percent of the increased metolachlor load measured between the extreme upstream and downstream sites on the Cedar River. The remaining 62 to 83 percent of the increased loads is attributed to input along the river's main stem. Ground-water discharge carrying atrazine and desethylatrazine is a likely source of some of the increased load detected in the river for two reasons: (1) Measurable increases of atrazine loads were associated only with those reaches of the river where discharge substantially increased because of ground-water discharge, (2) the mean concentrations of both atrazine (0.27 micrograms per liter) and desethylatrazine (0.11 micrograms per liter) in 15 shallow ground-water samples were equal to measured concentrations in the river 6 and 10 days after the ground-water samples were collected. The ground-water samples were collected from depths from 1 to 2 meters beneath the river bottom where the ground water was determined to be moving toward the river. The sources of atrazine and desethylatrazine detected in this ground water may include bank storage of riverwater, desorption of chemicals on sediment in the alluvial aquifer, or ground water originating at some distance from the river.

INTRODUCTION

Atrazine has been detected in large rivers throughout the year (Frank and others, 1982; Gilliom and others, 1985; Squillace and Engberg, 1988) and has been detected in rivers during periods of extended base flow (Squillace and Engberg, 1988). The source of water in the rivers during base flow is ground water and, perhaps, interflow during the early part of the recession curve on a discharge hydrograph (Linsley and others, 1975). Interflow is water that moves in the zone above the water table and reaches the stream channel after surface runoff has ceased. During base flow the source of atrazine, desethylatrazine (a degradation product of atrazine), and metolachlor in large river systems may be the tributaries or it may be input along the main stem of the river.

By defining where herbicides enter rivers during base flow, one may be able to determine the processes that are primarily responsible for the presence of herbicides in rivers during base flow. For example, if ground-water discharge to the main-stem river is thought to be an important contributor to the source of herbicides to the river, these herbicides should be found in the ground water and there should be a correlation between the ground-water discharge and the increased loads in the river. These increased herbicide loads will be isolated to the main-stem river. Loads, for this paper, is defined as the mass of a compound per unit time. If discharge from field drainage tile is a significant contributor to herbicides in large rivers, one would expect tributaries to be a major source of increased herbicide loads in the main-stem river. Drainage tiles are buried at a depth of 1 to 2 m (meters) to lower the water table in poorly drained soils. Discharge from the tiles eventually joins the tributaries and flows into the large rivers. The surface area drained by tributaries normally accounts for the largest area within the drainage basin and would, therefore, incorporate most of the discharge from field drainage tile. As another example, if herbicide loadings in the river are primarily the result of desorption from suspended sediment or bed sediment, one would expect the herbicide concentrations to increase along reaches of the river even where discharge does not significantly increase or is very small.

This paper describes where atrazine, desethylatrazine, and metolachlor enter the main stem of the Cedar River during base flow. The study area is a 116-km (kilometer) reach of the Cedar River located between Cedar Rapids and Conesville, Iowa (fig. 1). Atrazine, desethylatrazine, and metolachlor loads were determined for 27 accessible tributaries that have drainage areas greater than 5 square kilometers by measuring discharge and herbicide concentrations near the mouth of the tributaries. Four main-stem sites were selected to define any changes in the loads along the main stem of the Cedar River. The samples were collected after the river was in base-flow conditions for some time so that the effects of interflow would be minimal (fig. 2) on September 20-22, 1989.

RIVER CONDITIONS AND STUDY AREA

No storm runoff water entered the Cedar River during the period of study from September 20 through October 2, 1989. Examination of stream-discharge records for streams within the Cedar River basin shows that storm runoff generated in the extreme northern part of the basin takes about 10 days to travel to the basin outlet. The travel time from Cedar Rapids to Conesville is 2 to 2 1/2 days. The last significant rainfall in the basin prior to sampling occurred on September 7,8, and 9, 1989 (National Oceanic and Atmospheric Administration, 1989). This rain fell in the lower two-thirds of the basin. Therefore, there was ample time for any storm runoff to leave the basin by the time sampling began on September 20, 1989.

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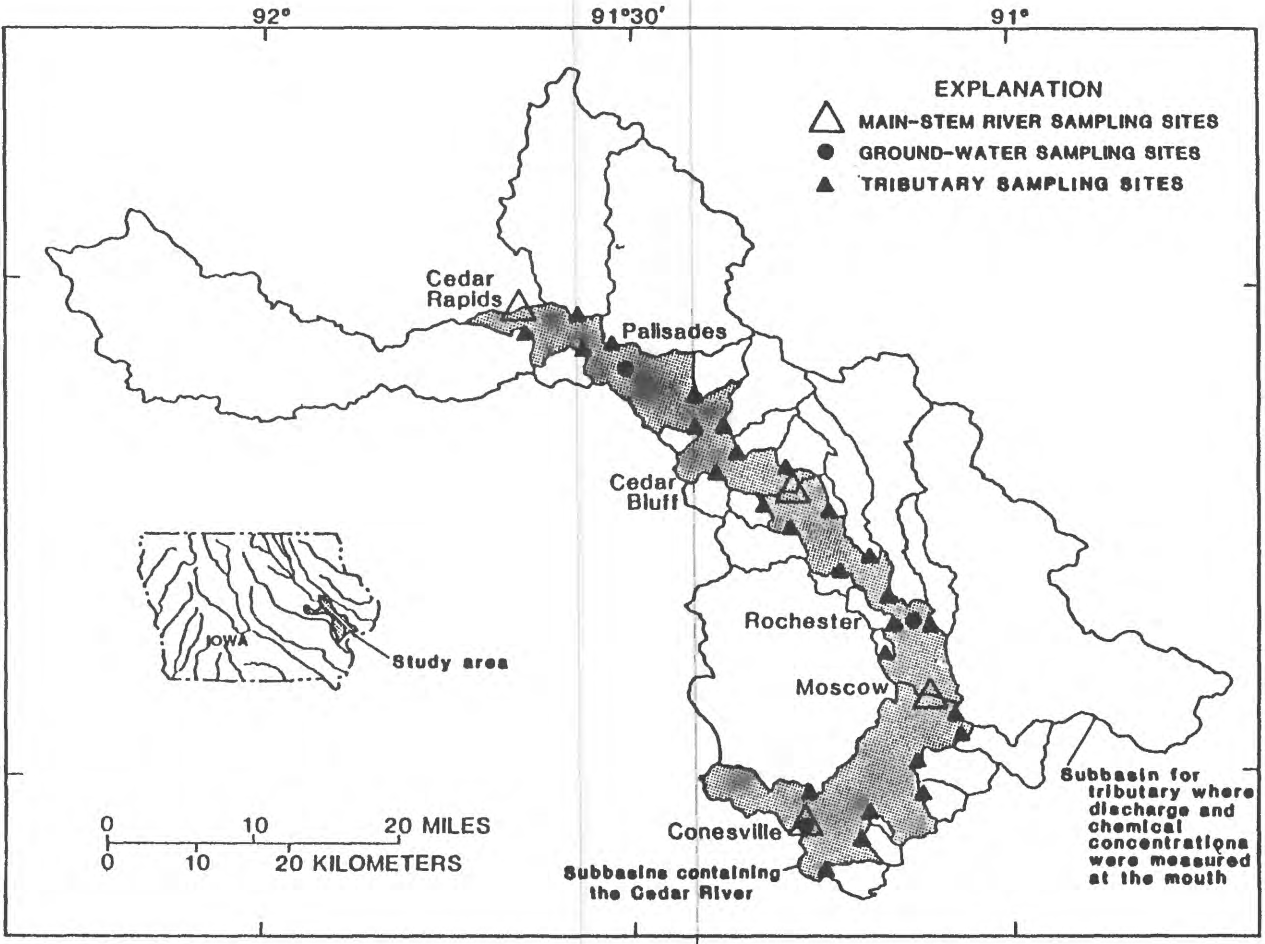
92°
91°30'
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42°
41°30'
EXPLANATION
△ MAIN-STEM RIVER SAMPLING SITES
● GROUND-WATER SAMPLING SITES
▲ TRIBUTARY SAMPLING SITES
Cedar Rapids
Palisades
Cedar Bluff
Rochester
Moscow
Conesville
IOWA
Study area
0 10 20 MILES
0 10 20 KILOMETERS
Subbasins containing the Cedar River
Subbasin for tributary where discharge and chemical concentrations were measured at the mouth

Figure 1. Cedar River study area with drainage basins where discharge and chemical concentrations were determined.

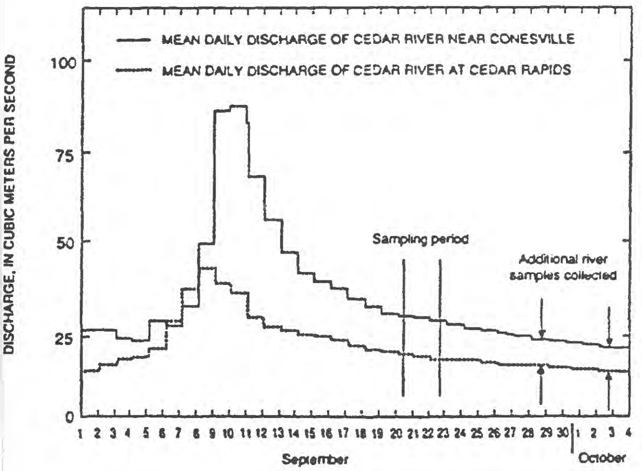

Figure 2. Dscharge of Cedar River at Conesville (downstream) and Cedar Rapids (upstream), September 2 to October 4, 1989, with sampling periods.

An alluvial aquifer is adjacent to the Cedar River and its width ranges from 0.5 to 4 km. Exposures along the river reveal that the aquifer is a fairly clean medium-grained quartz sand. This alluvial aquifer contains gravel and cobbles. Glacial drift adjacent to, and in some places beneath, the alluvial aquifer overlies Devonian- and Silurian-age bedrock aquifers.

Land use within the basin consists of 81 percent cropland, 7 percent pasture, and 12 percent forest and urban (U.S. Department of Agriculture, 1976). Corn and soybeans are the principal grain crops and are grown on more than 60 percent of the cropland (U.S. Department of Agriculture, 1976).

DATA COLLECTION AND CHEMICAL ANALYSIS

Water samples were collected in baked glass jars and filtered using baked Watmann[3] GF/F glass-fiber filters in a stainless-steel holder. The filters have a nominal pore size of 0.7 micrometers. Chemical analysis were done by gas chromatography/mass spectrometry and extraction of herbicides from the water samples was done by solid-phase cartridges (Thurman and others, 1990).

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[3] Use of trade names in this paper is for descriptive purposes only and does not constitute endorsement by the U.S. Geological Survey.

Surface-Water Samples

Stream discharges were measured by current meter (Buchanan and Somers, 1969). At each of the main-stem river sites, the discharge was measured three times during the sampling period. Discharge was measured once when the sample was collected from each of the tributaries.

Generally, whenever the Cedar River was sampled, a depth integrated (DI) sample was collected at the deepest and swiftest section of the river, and a composite sample collected from 10 equal-discharge sections across the river (equal discharge increment-EDI). Only EDI samples were collected for the tributaries.

Ground-Water Samples

The difference in head between the ground water and the river was measured with a modified minipiezometer described by Winter and others, (1988). The minipiezometer used for this study was constructed longer than described by Winter and others (1988) to allow ground-water samples to be collected at a depth of up to 2 m. A manometer similar to that described by Winter and others (1988) was used to measure the head difference between the ground water and the river.

Ground-water samples were collected at the Palisades site, near Rochester, Iowa, and at the Conesville streamflow gaging station (fig. 1). At each sampling site, the river width was divided into five sections and ground-water samples collected at 1 m depths. At the Palisades and Rochester sampling sites, additional ground-water samples were collected at a depth of 2 m at the left edge of the river (looking downstream).

RESULTS

Comparison of Equal Discharge Increment and Depth Integrated Samples

The differences in measured concentration between DI and EDI samples were compared using the paired t-test; they were not significantly different at the 95-percent confidence level, indicating that the sampling technique did not demonstrably affect the concentrations measured in the samples. The paired t-test was used because the differences in concentrations between pairs of DI and EDI samples in each group were normally distributed according to the Lilliefors test for normality at the 95-percent confidence level (Iman and Conover, 1983). Thirteen pairs of DI and EDI atrazine samples, 13 pairs of desethylatrazine samples, and 12 pairs of metolachlor samples were compared. Each pair of samples had been collected at the same site and time (within 1 hour). The average difference in concentration among the sample pairs was 0.016 μg/L (micrograms per liter) with a standard deviation of 0.050 μg/L, for atrazine; 0.0054 μg/L, with a standard deviation of 0.0095 μg/L, for desethylatrazine; and 0.0017 μg/L, with a standard deviation of 0.014 μg/L, for metolachlor.

Chemical Budget Analysis

A statistical summary of the budget analysis of the concentrations, discharges, and total herbicide loads in the Cedar River are shown in figure 3. Because the atrazine, desethylatrazine, and metolachlor concentrations are statistically the same among DI and EDI sample pairs, the averages of the values were used to calculate the total herbicide loads. The mean concentration of the herbicides at the sampling sites remained virtually unchanged from September 20 through September 22, 1989 (fig. 3). Both the t-test and the Mann-Whitney (nonparametric) test of the change in contaminant loads in the river showed that the total atrazine load increased significantly at the 95-percent confidence level between Cedar Rapids and Cedar Bluff, and between Moscow and Conesville. The total load for all three herbicides increased significantly at the 95-percent confidence level between Cedar Rapids and Conesville. The increases in loads between sampling sites are shown in figure 4.

Tributary Contributions

Concentrations of atrazine, desethylatrazine and metolachlor in the tributaries are less than those in the Cedar River (fig. 5). Tributaries contributed 25 percent of the increased atrazine load measured between Cedar Rapids and Cedar Bluff, and 13 percent of the increased atrazine load measured between Moscow and Conesville. Tributaries contributed 17 percent of the increased atrazine load, 24 percent of the desethylatrazine load, and 38 percent of the metolachlor load between Cedar Rapids and Conesville.

The small contribution of tributaries to the herbicide load in theCedar River (especially atrazine and desethylatrazine) indicates that field drainage tiles within the flood plain do not contribute most of the loads in the Cedar River. Tributaries drain 74 percent of the basin, whereas the remaining 26 percent of the basin lies primarily within the flood plain. If tiles are assumed to be uniformly distributed throughout the basin, tributaries should carry 74 percent of the tile discharge to the Cedar River. Because the data show that tributaries contribute only relatively small amounts of herbicides to the loads in the Cedar River, it would seem that the contribution of herbicides by tiles located within the flood plain would be minor. Furthermore, the flood-plain area may contain less drainage tiles than the rest of the basin, because it is difficult to locate drainage tile outlets (Iowa State University, Cooperative Extension Service, 1987). Tile drains in the flood plain may also be unnecessary, depending on the drainage characteristics of the soil (Schermerhorn and Highland, 1975; Schermerhorn, 1983; and Dankert, 1989).

Main-Stem Contribution

Most of the increased atrazine, desethylatrazine, and metolachlor loads probably directly enter the Cedar River in the ground-water discharge. Figure 3 shows that atrazine loads increase significantly when ground-water discharge to the Cedar River is large, as for example, between Cedar Rapids and Cedar Bluff, and between Moscow and

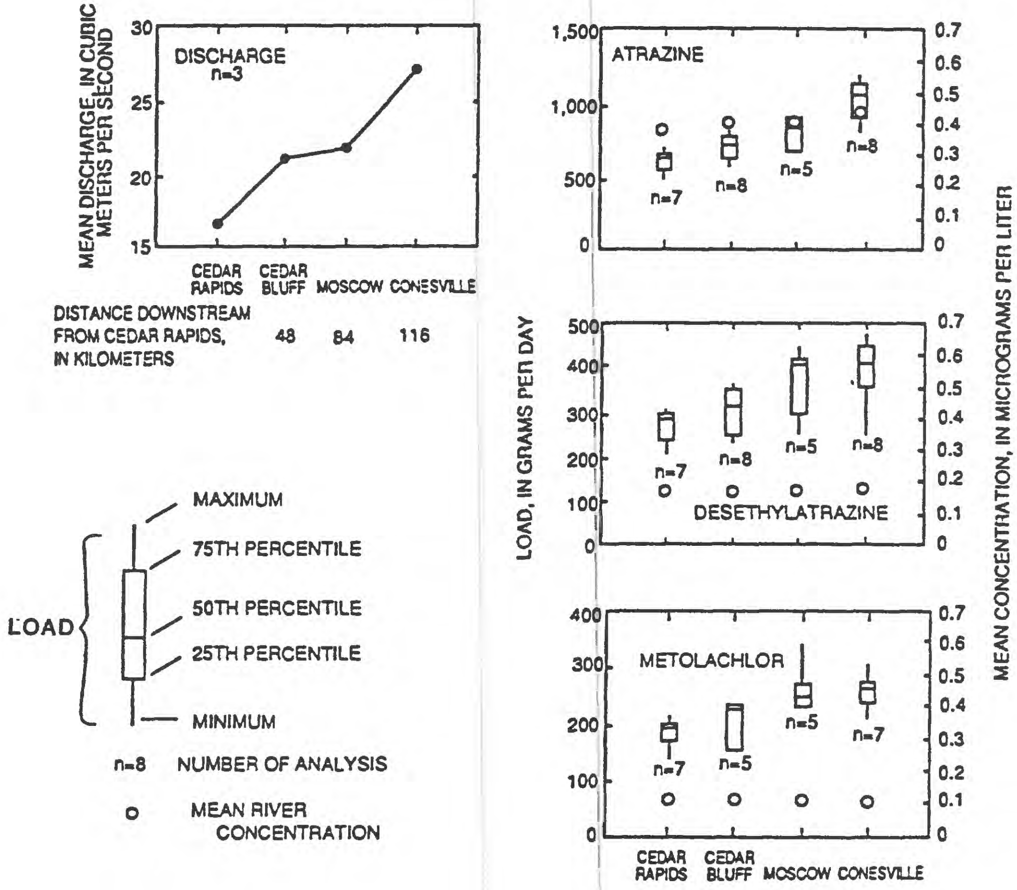

Figure 3. Statistical summary of discharge, atrazine, desethylatrazine, and metolachlor loads and concentrations, at the sampling stations on the Cedar River, September 20-22, 1989.

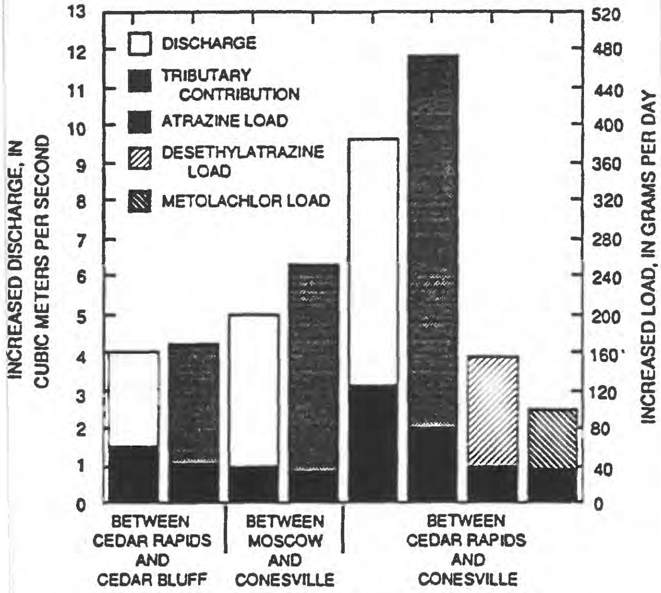

Figure 4. ncrease in discharge and statistically significant increases in load between the sampling stations on the Cedar River.

Conesville. This observation probably indicates that ground water is carrying these agricultural chemicals to the river. Contribution of atrazine in ground water caused a 21-percent increase in atrazine load between Cedar Rapids and Cedar Bluff and an additional 28-percent increase between Moscow and Conesville. By use of mass-balance calculations, the average atrazine concentration in the ground-water discharge between Moscow and Conesville would be about 0.6 to 0.7 μg/L during September 20-22, 1989.

Water in the Cedar River between Cedar Bluff and Moscow did not pick up significant amounts of agricultural chemicals from its interaction with the bed sediment. Discharge of the Cedar River between Cedar Bluff and Moscow does not significantly increase and, therefore, any changes in the herbicide loads in this reach would be caused by the interaction of river with the bed sediment. Because the atrazine, desethylatrazine, and metolachlor loads did not significantly increase between Cedar Bluff and Moscow (fig. 3) it seems that the interaction of the river with bed sediment is not a significant process in this reach of the river. Because atrazine has not been found on the suspended or bed

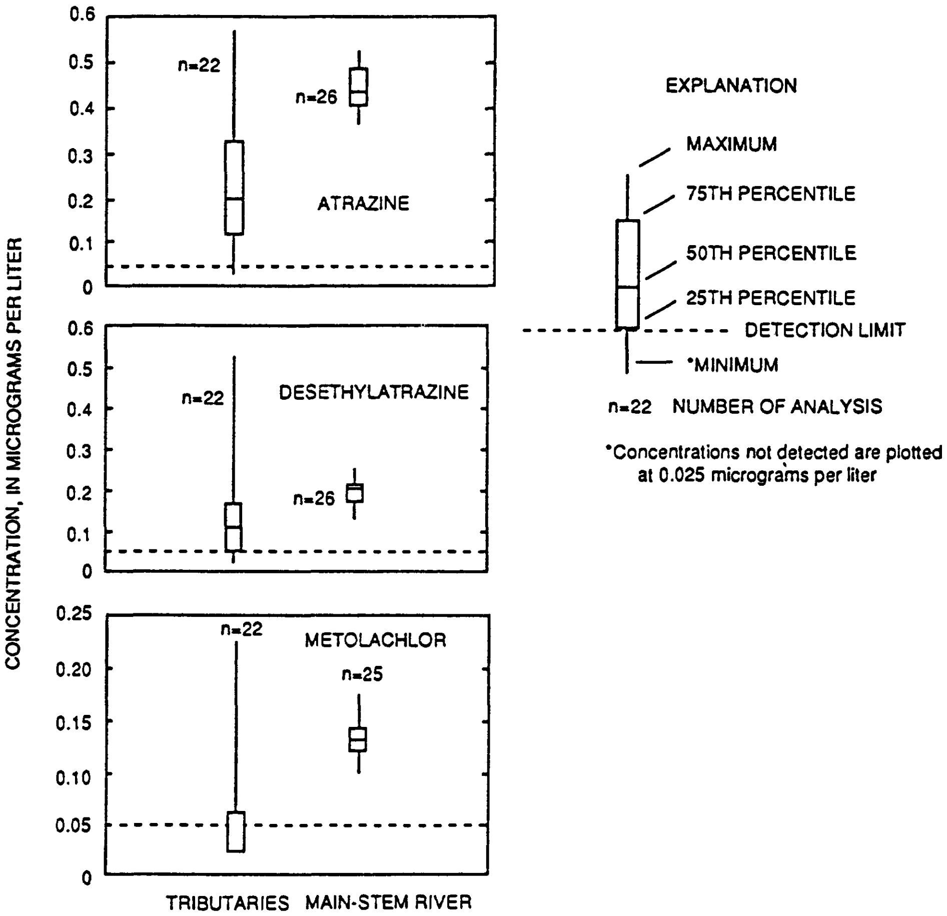

Figure 5. Statistical summary of the concentrations of atrazine, desethylatrazine, and metolachlor in tributaries and the main stem of the Cedar River, September 20-22, 1989.

sediment in many large river systems (Kennedy, 1978; Frank and others, 1979; Leung and others, 1982; and Gilliom and others, 1985) it would seem that the interaction of the river with bed sediment would not be significant in other reaches of the river.

Ground-Water Contribution

Fifteen ground-water samples were collected by the minipiezometer at depths of about 1.0 to 2.0 m below the riverbed where ground water was determined was to be moving toward the river by use of the manometer. The atrazine concentrations ranged from 0.05 to 0.46 ug/L, with a mean of 0.27 µg/L; desethylatrazine concentrations ranged from 0.05 to 0.33 µg/L, with a mean of 0.11 µg/L.

The mean atrazine and desethylatrazine concentrations in these ground-water samples are virtually equal to those measured in the river 6 and 10 days after the last ground-water samples were collected. The river was sampled at Cedar Rapids and Conesville on September 28, 1990, and on October 2, 1990, after the collection of the ground-water samples (fig. 2). The atrazine and desethylatrazine concentrations in these samples ranged from 0.20 to 0.28 µg/L, and from 0.12 to 0.14 µg/L, respectively.

Estimates of ground-water velocities within the riverbed support the relation of ground water of the minipiezometer samples with that of the river about 6 days later. The mean of 17 ground-water gradients measured by minipiezometers was 0.007. The bed material is a clean medium-grained sand with an estimated vertical hydraulic conductivity of 10 m/d (meters per day). The porosity of these poorly compacted sands is estimated to be 0.40. With these estimated values, the velocity is calculated to be about 0.18 m/d, meaning that it would take about 6 days for ground water 1 m deep to reach the river. Furthermore, assuming these same aquifer characteristics, the amount of water stored in the upper 1 m of the riverbed is sufficient to supply the ground water that discharges to the river for a period of 5 to 7 days.

Desorption of atrazine and desethylatrazine from the alluvial aquifer is a possible source of contamination to the ground water but this desorption process, if it occurs, is probably not a significant source of contamination. Organic material and some inorganic mineral surfaces have been shown to be important sites for the sorption of some organics (Schwarzenbach and Westall 1981; Karickhoff, 1984; and Mackay and others, 1986). However, atrazine has not been found on the suspended sediment or bed sediment in large rivers systems (Kennedy, 1978; Frank and others, 1979; Leung and others, 1982; and Gilliom and others, 1985). The high mobility of desethylatrazine in the soil (Muir and Baker, 1978) and the solubility of metolachlor indicate that sorption of these chemicals is even less likely than it is for atrazine.

Bank storage of runoff water or shallow ground water in the alluvial aquifer may be a more likely source of herbicides to the river after a runoff event. The concentrations of atrazine, desethylatrazine, and metolachlor in the river declined between September, 20-22, 1989, to September 28, 1989, but stabilized between September 28 and October 2, 1989. The higher concentrations that were measured September 20-22, 1989, may have been the result of the release of atrazine, desethylatrazine, and metolachlor from bank storage. A rise in the river stage is necessary for riverwater to enter the alluvial aquifer. After normal ground-water gradients are reestablished, water and herbicides stored within alluvial aquifer return to the river. However, the organic carbon in the alluvial aquifer or the bed sediment may retard the movement of dissolved organics (Schwarzenbach and Westall, 1981; Schwarzenbach and others, 1983; and Winters and Lee, 1987).

During periods of extended base flow, when runoff events are very infrequent, atrazine is still detected in large rivers (Squillace and Engberg, 1988). At these times, herbicides that were applied in the basin some distance from the river later enter the river in ground-water discharge. The concentrations of herbicides detected in the Cedar River on September 28 and October 2, 1989, stabilized and are similar to those detected in the river during other periods of extended base flow (Squillace and Engberg, 1988).

SUMMARY

During base-flow conditions, tributaries contributed 17 percent of the increased atrazine load, 24 percent of the increased desethylatrazine load, and 38 percent of the increased metolachlor load measured between the extreme upstream and downstream sites on the Cedar River. The remaining increased load is attributed to input along the main stem of the river. The interaction of the river with the bed sediment does not seem to cause significant increases in the river loads. However, the increased atrazine and desethylatrazine loads are related to the ground water discharge to the river for two reasons: (1) Measurable increases of atrazine loads were associated only with those reaches of the river where discharge substantially increased because of ground-water discharge, and (2) the mean concentrations of atrazine and desethylatrazine in 15 shallow ground-water samples were equal to measured concentrations in the river 6 and 10 days after the ground-water samples were collected. The sources of atrazine and desethylatrazine in this ground water may include desorption of chemicals from the sediment within the riverbed or the alluvial aquifer, release of runoff water from bank storage, or recharge of contaminated water to the alluvial or bedrock aquifers some distance from the river. Because previous work has shown that atrazine is not commonly found in the bed sediment or suspended sediment in large river systems, it would seem that the release of contaminated water from bank storage or the discharge of contaminated ground water from parts of the basin some distance from the river are the most important causes of input of these agricultural chemicals to the river during base flow.

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THE EFFECT OF SURFACE-WATER AND GROUND-WATER EXCHANGE ON THE TRANSPORT AND STORAGE OF ATRAZINE IN THE CEDAR RIVER, IOWA

By Michael J. Liszewski [1] and Paul J. Squillace [1]

ABSTRACT

The transport and storage of atrazine was studied in the Cedar River and an adjacent alluvial aquifer in eastern Iowa. River samples were collected monthly during low-flow conditions from May through December 1989, and daily during the rise and fall of river stage caused by storm runoff in March 1990. Water samples were collected from 23 wells completed in the aquifer in a vertical plane 150 meters long by 15 meters deep and perpendicular to the river. The wells were sampled five times during low-flow conditions of the Cedar River during 1989 and three times over the rise and fall of the river stage caused by storm runoff in 1990.

Atrazine concentrations in the Cedar River ranged from 0.12 micrograms per liter during extended low-flow conditions beginning in July 1989 to 0.82 micrograms per liter during peak river stage in March 1990. Atrazine concentrations in samples from wells in the alluvial aquifer ranged from less than 0.05 to 0.68 micrograms per liter during the period of study. In general, atrazine concentrations were stratified in the alluvial aquifer with larger concentrations occurring near the top. The period of high river stage in March 1990 correlates with large concentrations of atrazine in samples from wells less than 30 meters from the river. Concentrations of atrazine in samples from the wells greater than 30 meters from the river did not correlate to the high river stage.

The observed data may be explained by the exchange of surface water and ground water in the adjacent alluvial aquifer as a result of changes in river stage during periods of storm runoff and low flow. The data indicate that the alluvial aquifer may act as a reservoir of atrazine. During storms, areas of the aquifer closest to the river are recharged with riverwater containing atrazine, which may later return to the river during low flow. Water-table gradients and specific-conductance measurements provide evidence for (1) a large ground-water component in streamflow during low-flow conditions, and (2) the presence of infiltrated riverwater in the aquifer during high river stage.

INTRODUCTION

Nonpoint source loads of agricultural chemicals are an important water-quality concern in Iowa. The public is exposed to these chemicals most commonly in water supplied by municipal water departments that draw from surface-water or shallow ground-water sources. Many municipalities use surface water directly or surface water that infiltrates alluvial aquifers, which filter the water as a preliminary step in water treatment before distribution. The processes affecting the water quality of these important sources of water are of concern to water users.

Agricultural chemicals originate in areas where they are applied directly to the land surface to control weeds and insects. Water, generally in the form of precipitation, extracts the chemicals from the soil environment, mobilizes them, and transports them deeper into the soil horizon and to streams that drain the basin. Atrazine concentrations larger than 0.1 μg/L (micrograms per liter) have been observed in the Cedar River throughout the year (Squillace and Engberg, 1988). Once transported to a stream, dynamic ground- and surface-water processes are responsible for storage and further distribution of atrazine in the environment. One important process may be the exchange of surface-water and ground water in adjacent alluvial aquifers during periods of storm runoff and low flow. As river stage rises in response to snowmelt and rain runoff, gradients in alluvial aquifers are reversed and surface water containing large concentrations of agricultural chemicals may infiltrate the aquifer. During subsequent low-flow conditions, a water-table gradient toward the river is established and the chemicals in ground water may reenter the stream. The extent of infiltration has not been measured.

This paper documents some of the results of investigations conducted during 1989 and 1990 to assess the transport into, and storage of atrazine in alluvial aquifers caused by bank storage of riverwater. Bank storage occurs during periods of storm runoff when the river stage is high. Wells have been installed in an alluvial aquifer adjacent to the Cedar River in east-central Iowa so that the spatial distribution of atrazine can be measured during various flow regimes. The wells were sampled five times during low-flow conditions and three times during a period of storm runoff. River samples were collected monthly during low-flow conditions and daily during periods of storm runoff. Analytical results for atrazine and specific conductance are presented here from wells less than 150 m (meters) from the river. These wells appeared to be the most likely to yield riverwater that infiltrated during the spring 1990 storm.

Location and Description of Study Area

The study area is located in an unfarmed flood plain of the Cedar River in east-central Iowa (fig. 1). At this site, the Cedar River drains approximately 10,475 square kilometers of mostly farmed land. The average discharge is 97.6 cubic meters per second (U.S. Geological Survey, 1989). The alluvium along the river channel consists of fine- to medium-grained sand, 15 m thick, which decreases in thickness with distance from the river. Exploratory drilling shows that the alluvium is underlain by 15 m of dense till overlying carbonate bedrock. The low-permeable till may hydraulically isolate the alluvial aquifer from the underlying bedrock. The riverbank is approximately 4 m high at the water's edge during low-flow conditions, and slopes gently downhill from the river (fig. 2). The water table is typically 3 to 5 m below land surface, and its gradient is toward the river during low-flow conditions.

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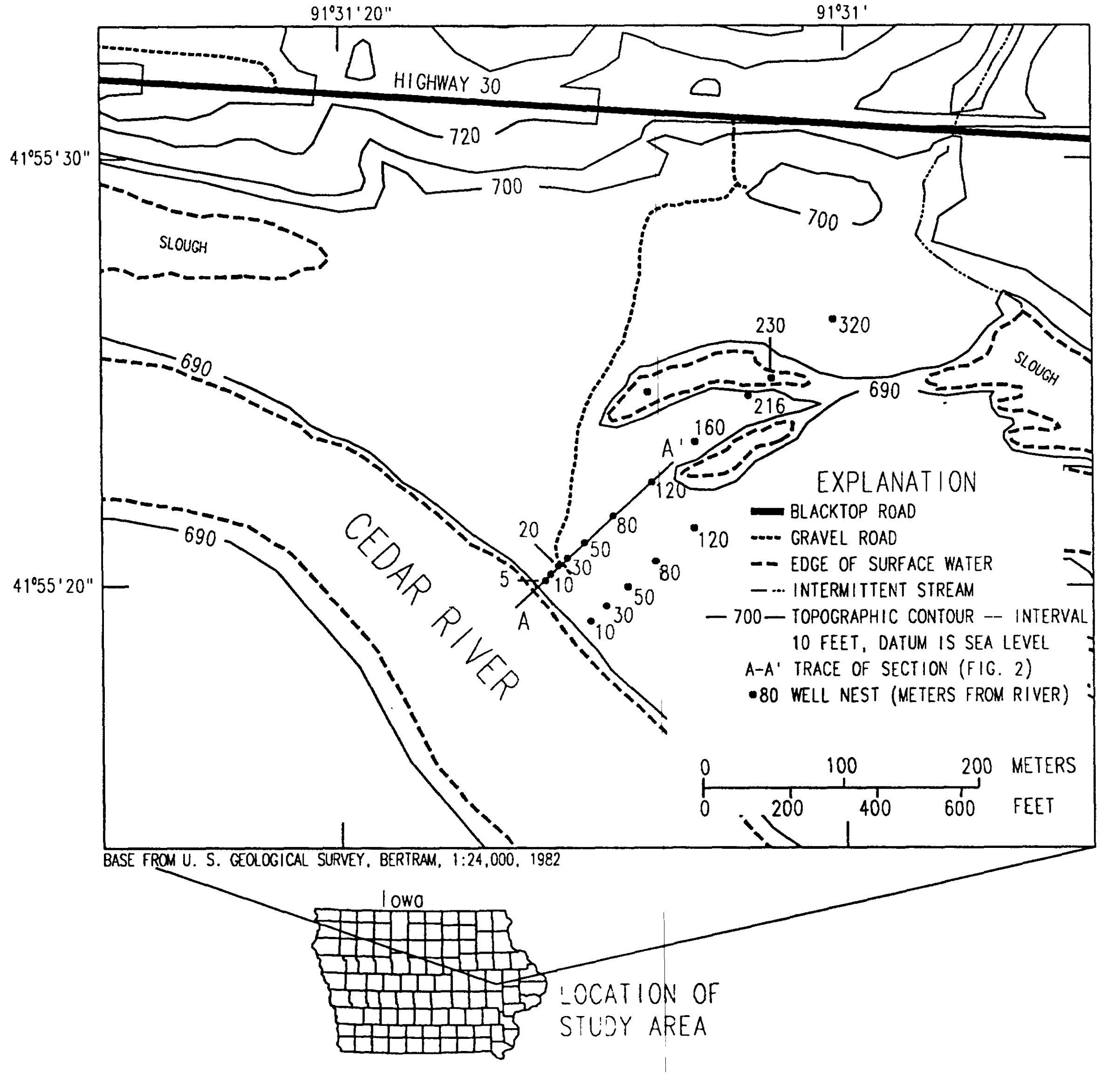
91°31'20"
91°31'
41°55'30"
41°55'20"
HIGHWAY 30
720
700
700
SLOUGH
690
690
690
SLOUGH
CEDAR RIVER
230
•320
•216
160
A'
120
80
50
30
10
20
5
A
•120
•80
•50
•30
•10
EXPLANATION
BLACKTOP ROAD
GRAVEL ROAD
EDGE OF SURFACE WATER
INTERMITTENT STREAM
—700— TOPOGRAPHIC CONTOUR -- INTERVAL 10 FEET, DATUM IS SEA LEVEL
A-A' TRACE OF SECTION (FIG. 2)
•80 WELL NEST (METERS FROM RIVER)
0 100 200 METERS
0 200 400 600 FEET
Iowa
LOCATION OF STUDY AREA

BASE FROM U. S. GEOLOGICAL SURVEY, BERTRAM, 1:24,000, 1982

Figure 1. Study area along the Cedar River in east-central Iowa.

Sample Collection and Analysis

Thirty-three observation wells were installed in the alluvium in a series of nests adjacent to the Cedar River in a vertical plane 320 m long and 15 m deep perpendicular to the river. The wells were drilled with a 15.2-cm (centimeter) -outside-diameter hollow-stem auger drill rig. Fifteen additional wells were installed in a plane 50 m south of and parallel to the first plane to help define the flow system at the study site (fig. 1). Wells were constructed of 5.1-cm-outside-diameter polyvinyl chloride pipe with 60-cm-long slotted screens at the bottom. The annulus around the well was backfilled with alluvium and was plugged with bentonite near the surface.

Wells were sampled five times during May through December 1989 and three times during February through April 1990. Samples were collected approximately monthly during 1989, whereas sampling in 1990 was timed for specific intervals during the rising and falling river stage of a period of storm runoff. Shallow wells (less than 4 m from the land surface) could not be sampled when the water table dropped below the screened interval of the well. For the period of storm runoff, well samples were collected before the river began to rise, during the peak stage of the river, and after the river had receded to low flow. The runoff event

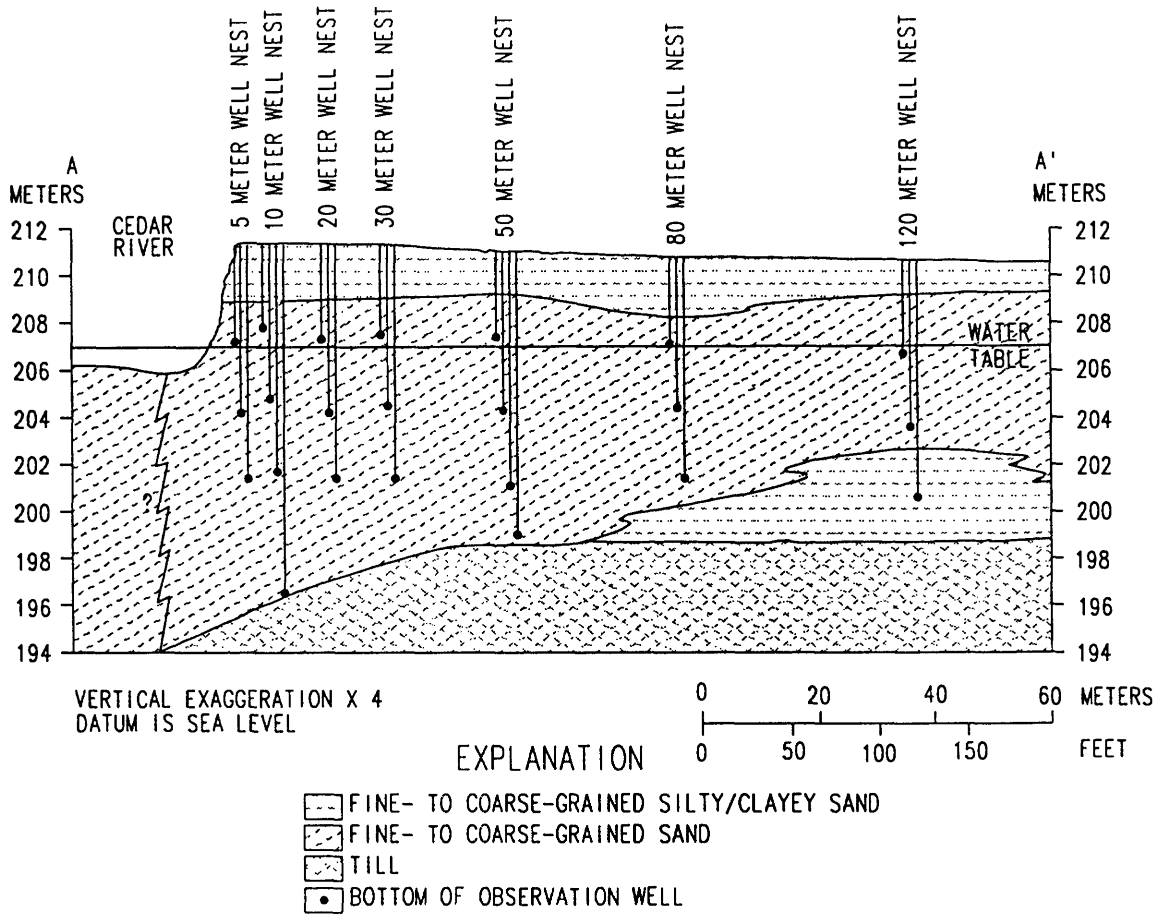
A
METERS
212
210
208
206
204
202
200
198
196
194
CEDAR RIVER
5 METER WELL NEST
10 METER WELL NEST
20 METER WELL NEST
30 METER WELL NEST
50 METER WELL NEST
80 METER WELL NEST
120 METER WELL NEST
A'
METERS
WATER TABLE
?
VERTICAL EXAGGERATION X 4
DATUM IS SEA LEVEL
0 20 40 60 METERS
0 50 100 150 FEET
EXPLANATION
FINE- TO COARSE-GRAINED SILTY/CLAYEY SAND
FINE- TO COARSE-GRAINED SAND
TILL
BOTTOM OF OBSERVATION WELL

Figure 2. Geologic section A-A' (fig. 1) showing locations of observation wells.

occurred in March 1990 before spring application of fertilizers and herbicides. Samples were collected at the screened interval using a stainless steel submersible pump with Teflon[2] tubing. During 1989, wells were purged a minimum of three well volumes; the pump was positioned just below the water table. Prior to 1990, a packer was installed above the pump intake to reduce the amount of water needed for purging. Twenty liters of purged water were pumped from each well with this configuration to equilibrate sampling equipment and field instruments.

Surface-water samples were collected with a vertically integrating hand sampler in the deepest, swiftest part of the stream. Sampling equipment was decontaminated with deionized water filtered through activated-carbon filters to remove residual organic compounds. A rigorous quality-control and quality-assurance program accompanied the sample collection (P.J. Squillace and M.J. Liszewski, U.S. Geological Survey, written commun., 1991).

Samples were analyzed for common herbicides, nitrate, and field properties. Herbicide samples were filtered through a nominal 0.7-micrometer glass fiber filter in a stainless steel filter holder and collected in 125 milliliter glass jars with Teflon-lined caps. The glass fiber filters and glass jars were heated to 450 °C (degrees Celsius) for 4 hours to remove residual organic compounds. Herbicides were isolated from the water by solid-phase extraction and analyzed by gas chromatography/mass spectrometry (Thurman and others, 1990). Specific conductance was measured by immersing probes into a flow-through chamber containing continuously pumped well water.

RESULTS OF ANALYSIS

Atrazine-concentration and specific-conductance data for the Cedar River are compared to the daily mean stage of the river for the period of study and shown in figure 3. The largest atrazine concentrations were measured in the postapplication period, May and June 1989. Interpretation of these data is difficult because of insufficient background data up to this time. The riverwater was likely responding to spring runoff containing larger concentrations of the herbicide, which was applied in early May.

Beginning in July 1989, low-flow conditions generally prevailed in the river until March 1990. During this period, atrazine concentrations ranged from 0.12 µg/L to 0.82 µg/L.

[2] Use of brand or trade names in this paper is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

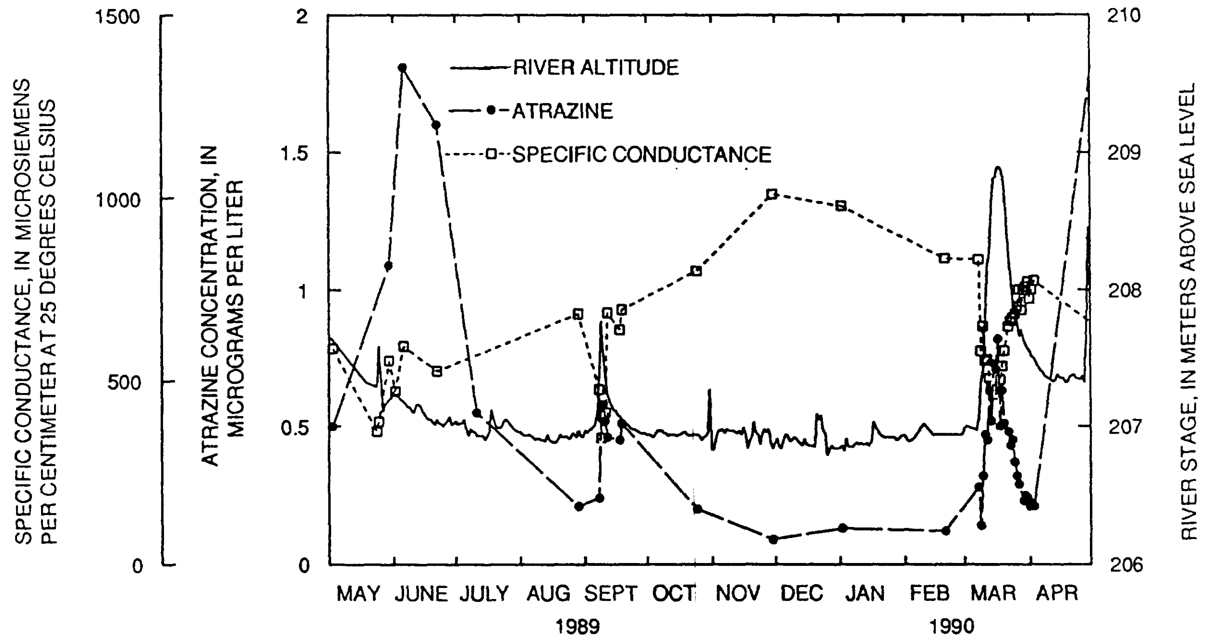

Figure 3. Cedar River stage, atrazine concentration, and specific conductance at the study area (fig. 1), May 1989 through April 1990.

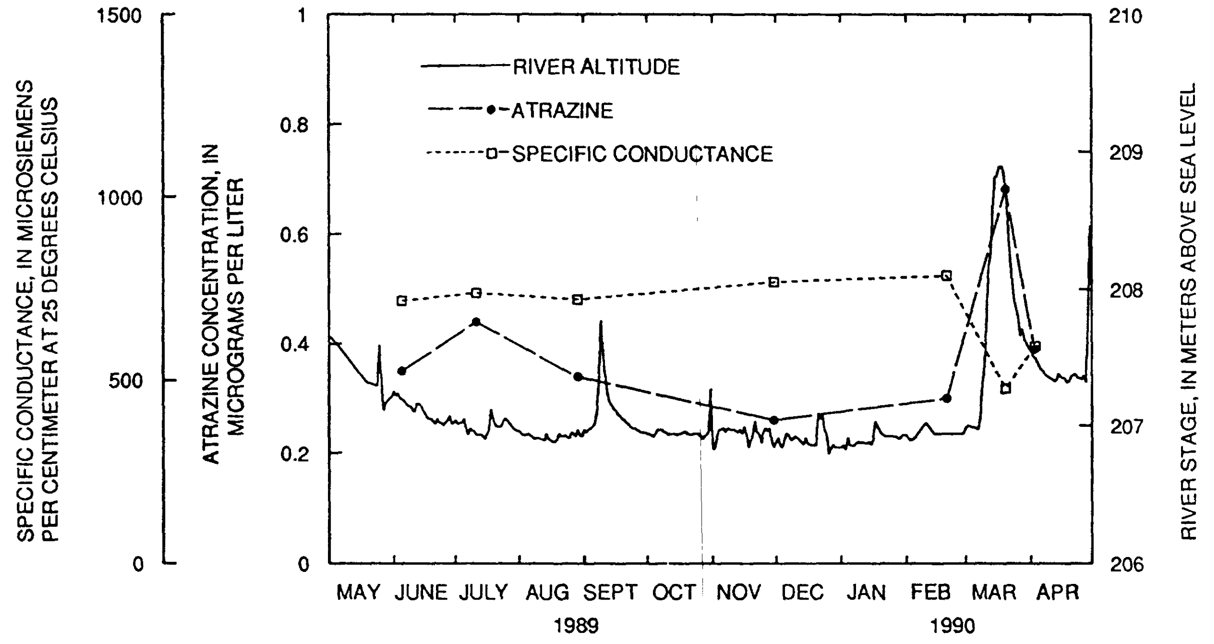

Figure 4. Cedar River stage and atrazine concentration and specific conductance in samples from an alluvial well located 10 meters from the river at a depth 6 meters below land surface (fig. 2).

The maximum concentration during this period was measured during the peak river stage caused by storm runoff in March 1990. Specific conductance ranged between 343 and 1,011 µS/cm (microsiemans per centimeter) at 25 °C over the same period. In contrast to atrazine concentrations, specific conductance was greatest during periods of low river stage but decreased sharply during peak river stage. Decreased specific conductance during peak river stage probably resulted from a reduction in the ground-water component of the river, whereas large atrazine concentrations probably resulted from scouring of the land surface during periods of storm runoff.

Atrazine concentrations in samples from wells completed in the alluvial aquifer ranged from less than 0.05 ug/L (the detection limit) to 0.68 µg/L during the period of study. In general, atrazine concentrations were stratified in the aquifer; the largest concentrations were found near the top of the aquifer. The period of higher river stage in March 1990 correlates with the increased concentrations of atrazine in samples from wells less than 30 m from the river. For example, atrazine concentrations in samples from a selected well located 10 m from the river with a screened interval 6 m below the land surface (fig. 2) increased from 0.30 µg/L in February 1990 to 0.68 µg/L in March 1990 as the river stage increased 2 m (fig. 4). However, atrazine concentrations in

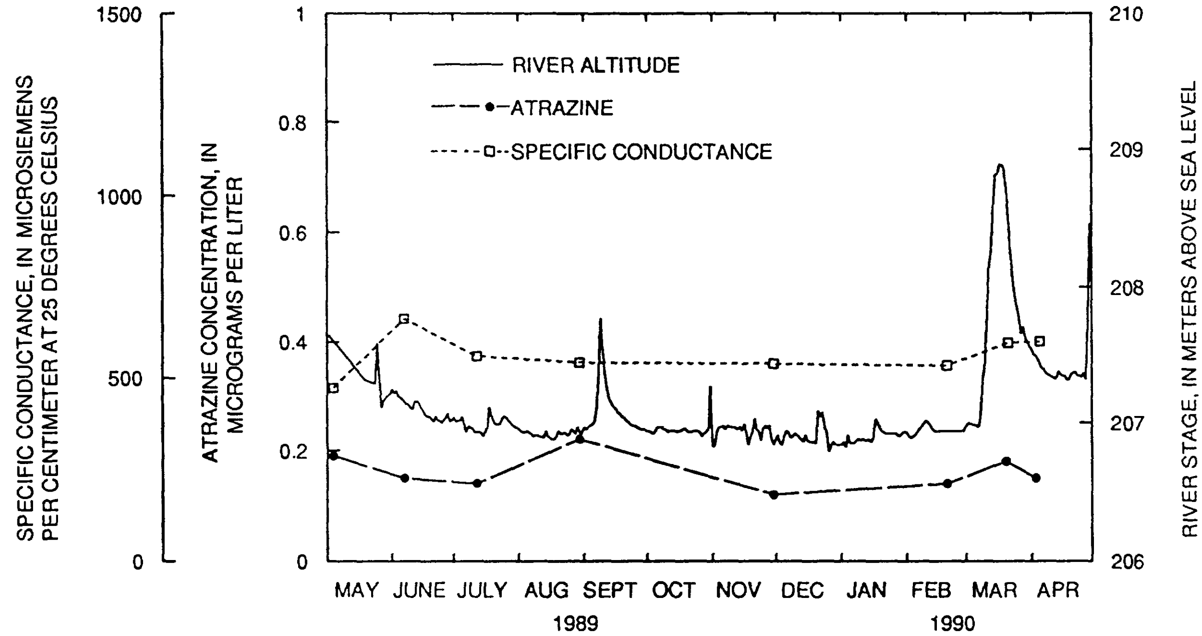

Figure 5. Cedar River stage and atrazine concentration and specific conductance in samples from an alluvial well located 80 meters from the river at a depth 6 meters below the land surface (fig. 2).

samples from a selected well located 80 m from the river with a screened interval 6 m below the land surface (fig. 2) increased only slightly from 0.14 µg/L to 0.18 µg/L during the same period (fig. 5). Large concentrations of atrazine were found in samples from shallow wells (screened intervals less than 4 m below land surface) beyond 30 m from the river. However, water from some of these wells also had larger concentrations of atrazine than deeper wells before the rise in river stage and some wells could not be sampled during low-flow conditions. Specific conductance of water samples from wells less than 30 m from the river were inversely related to variations in river stage and atrazine concentration. Specific conductance of samples collected in wells farther than 30 m from the river did not respond to variations in river stage during this period. Spatial changes in atrazine and specific-conductance measurements for the three samplings of the alluvial aquifer during the storm are illustrated in geologic section A-A′ (figs. 6 and 7).

EFFECT OF GROUND WATER AND STORM RUNOFF ON ATRAZINE IN STREAMFLOW

Extensive alluvial aquifers are common along most of the Cedar River main stem and extend hundreds of meters away from the river. The river can either recharge or drain the aquifer. During low-flow conditions, ground water discharges to the river and leaves the basin. The Cedar River basin received less-than-normal precipitation during 1989. The mean discharge of the Cedar River at Cedar Rapids (located approximately 25 kilometers northwest of the study area) during water year 1989 was only 29 percent of the mean discharge over the last 87 years (U.S. Geological Survey, 1989). In early September 1989, the river stage increased because of a brief but intense rainstorm. The relatively large specific conductance measured in the Cedar River during most of 1989 is evidence of the large contribution of ground water to the river (Hem, 1989). Assuming the alluvial aquifer studied here is typical of other alluvial aquifers, the sustained large concentrations of atrazine observed in the river throughout the period of extended low flow may be partly explained by release of atrazine stored in the aquifer.

Data from the brief periods of increased river stage during 1989 show the effects of wet climatic conditions on the chemistry of the river relative to atrazine and specific conductance. The wet spring of 1990 contrasts with the generally dry spring of 1989. A large storm occurred in mid-March of 1990. The stage of the Cedar River at the study site rose steadily for 2 weeks and peaked at a stage 2 m higher than the stage before the storm. The storm runoff caused an increase in concentrations of atrazine in the river while decreasing the specific conductance. During this period, water-table gradients in the alluvial aquifer sloped away from the river (reverse gradient), providing hydrologic evidence of riverwater infiltration into the alluvial aquifer. The infiltration of riverwater when river stage rose caused larger increases in atrazine concentrations in water samples from wells in the alluvial aquifer less than 30 m from the river than in water samples from wells that are more distant. Decreased specific conductance in samples from wells close to the river provides additional evidence for the presence of infiltrated streamwater in the aquifer. Concentrations of atrazine decreased in wells less than 30 m from the stream after the river stage receded to low-flow stage but remained larger than before the rise. Transport of infiltrated chemicals within the aquifer may be preventing the immediate discharge of the chemicals in the ground water back to the river, and may be spatially distributing them within the aquifer where they become stored for later release.

SUMMARY

Surface-water and ground-water exchange may be important to understanding the transport and storage of atrazine in fluvial systems. The existence of a dynamic interchange of water between the river and its adjacent

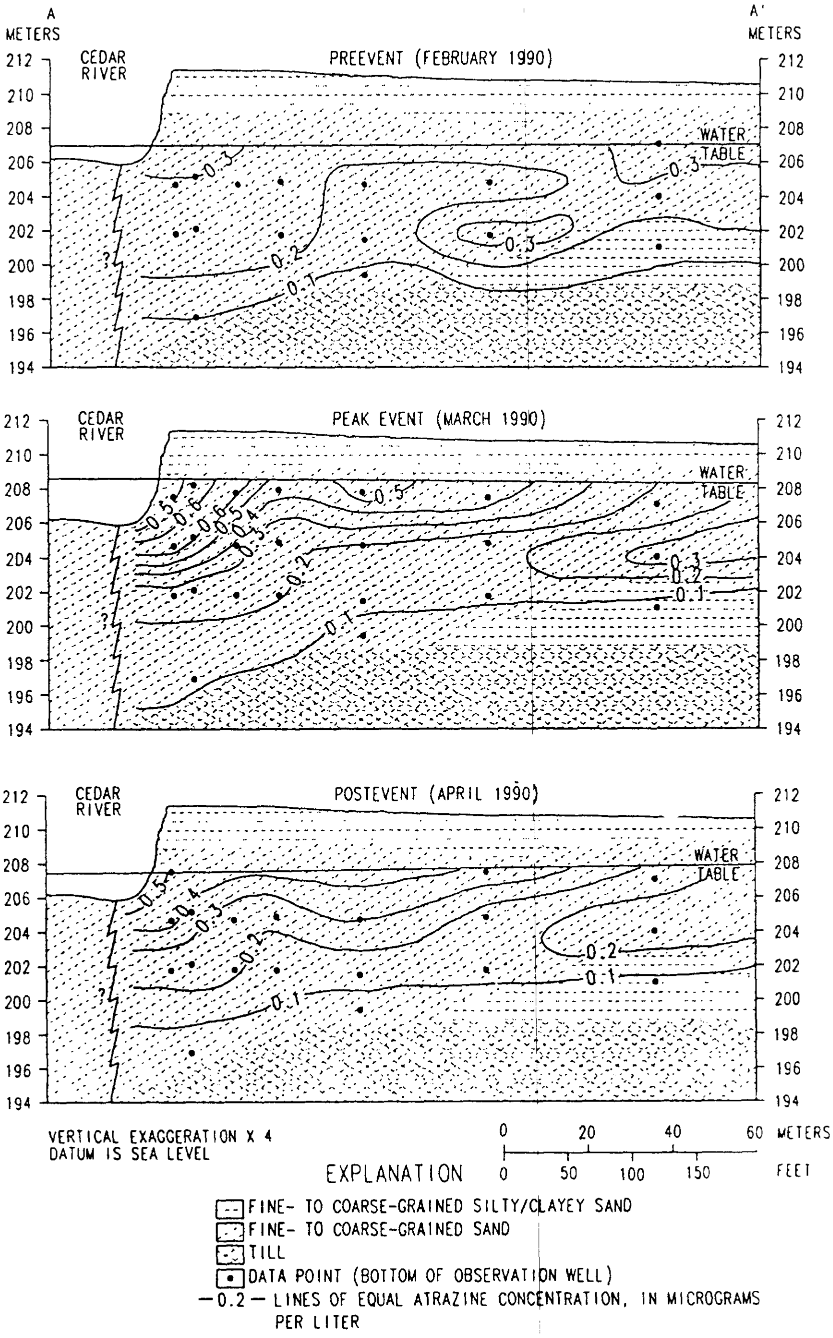
A
METERS
A'
METERS
CEDAR RIVER
PREEVENT (FEBRUARY 1990)
WATER TABLE
212
210
208
206
204
202
200
198
196
194
?
0.3
0.3
0.3
0.2
0.1
PEAK EVENT (MARCH 1990)
0.5
0.6
0.55
0.5
0.4
0.3
0.2
0.1
0.3
0.2
0.1
POSTEVENT (APRIL 1990)
0.5
0.4
0.3
0.2
0.1
0.2
0.1
VERTICAL EXAGGERATION X 4
DATUM IS SEA LEVEL
0
20
40
60 METERS
0
50
100
150 FEET
EXPLANATION
FINE- TO COARSE-GRAINED SILTY/CLAYEY SAND
FINE- TO COARSE-GRAINED SAND
TILL
DATA POINT (BOTTOM OF OBSERVATION WELL)
—0.2— LINES OF EQUAL ATRAZINE CONCENTRATION, IN MICROGRAMS PER LITER

Figure 6. Cross-sectional distribution of atrazine in geologic section A-A' at preevent, peak event, and postevent flow conditions during a period of storm runoff in the spring of 1990.

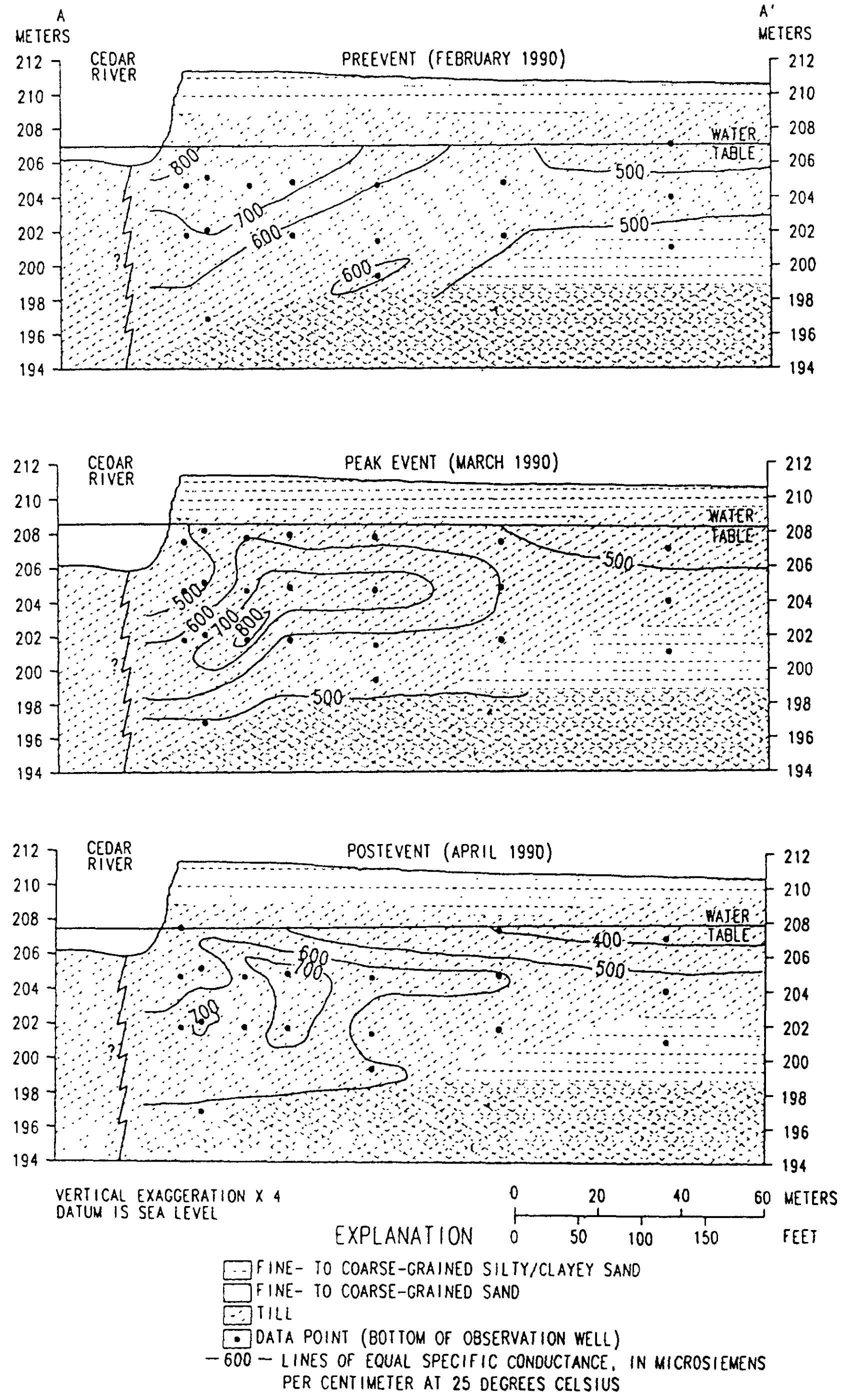
A
A'
METERS
CEDAR RIVER
PREEVENT (FEBRUARY 1990)
WATER TABLE
800
700
600
500
?
PEAK EVENT (MARCH 1990)
POSTEVENT (APRIL 1990)
400
212
210
208
206
204
202
200
198
196
194
VERTICAL EXAGGERATION X 4
DATUM IS SEA LEVEL
0 20 40 60 METERS
0 50 100 150 FEET
EXPLANATION
FINE- TO COARSE-GRAINED SILTY/CLAYEY SAND
FINE- TO COARSE-GRAINED SAND
TILL
DATA POINT (BOTTOM OF OBSERVATION WELL)
—600— LINES OF EQUAL SPECIFIC CONDUCTANCE, IN MICROSIEMENS PER CENTIMETER AT 25 DEGREES CELSIUS

Figure 7. Cross-sectional distribution of specific conductance in geologic section A-A' at preevent, peak event, and postevent flow conditions during a period of storm ruhoff in the spring of 1990.

alluvial aquifer has implications for the overall distribution of agricultural chemicals within the environment. This study shows that part of the aquifer is recharged with infiltrating streamwater that contains large concentrations of atrazine. The atrazine is stored in the aquifer and released slowly to the river during low-flow conditions. This exchange of water is likely responsible for the presence of atrazine observed in the alluvial aquifer and the sustained concentrations in the surface water throughout the year. These processes serve to distribute atrazine within the environment and retard its transport out of the basin.

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DISSIPATION OF STARCH-ENCAPSULATED HERBICIDES: A FIELD COMPARISON WITH POWDERED HERBICIDES

By M. S. Mills[1], E. M. Thurman[1], R. E. Wing[2], and P. L. Barnes[3]

ABSTRACT

A dissipation study of atrazine and alachlor in starch-encapsulated and powdered forms was conducted on two adjacent corn plots at the Silver Lake Experimental Field Site, near Topeka, Kansas. A 30-percent difference in the total mass of herbicide washed from the plots was observed and attributed to the different release patterns of the two herbicide forms. The distribution of mass of starch-encapsulated herbicide released in runoff water throughout the growing season followed a normal-distribution-shaped curve, whereas the powdered-herbicide runoff water had a high mass present at the start of the season, which decreased in an exponential manner through time. Atrazine and alachlor were released slowly from the starch-encapsulating matrix as it expanded in the presence of water, and only a small mass of herbicide was present at any time for washoff, throughout the entire runoff season. Because of this slow release of starch-encapsulated herbicides, the initial flush of large concentrations of herbicides from fields could be reduced by a factor of approximately 20, and decrease the total mass of herbicide washed from the field by 30 percent. Furthermore, the slow release of encapsulated herbicides should extend the residence time of the parent herbicide in the microbially active topsoil zone, which enhances biological and chemical degradation to less-active metabolites while maintaining weed control.

INTRODUCTION

The volatile, soluble, and persistent nature of the two most extensively used preemergent herbicides, atrazine and alachlor, contributes to their mobility in the environment. As a consequence, degradation of surface and ground water resulting from agricultural practices centered in the "Corn Belt" of the United States recently has received widespread publicity (Holden, 1986; Fairchild, 1987; Leonard, 1988; Libra and others, 1987; Pereira and Rostad, 1990; Baker and Richards, 1990; Buser, 1990; E.M. Thurman and others, in press). Despite documented problems and the need to maintain successful farming practices and avoid economic hardship, herbicides probably will remain a primary method of weed control for the forseeable future (Sun, 1986). Unless improved management systems are devised, the potential environmental hazards of herbicide use will continue, regardless of point or nonpoint sources.

The concept of encapsulating herbicides for their controlled release into the environment has been well established in the literature, and the technology for a starch-encapsulated matrix has developed rapidly over the last decade (Wing and others, 1987; Schreiber and others, 1988). The insoluble starch matrix expands on contact with moisture, and small amounts of herbicide are released slowly through time. Laboratory studies conducted to assess release characteristics indicate that encapsulated formulations are superior in performance to nonencapsulated formulations in reducing evaporative and degradative losses (Schreiber and others, 1978), extending herbicidal activity (Coffman and Gentner, 1980), reducing leaching (Baur, 1980), and decreasing dermal toxicity of the active ingredient (Riley, 1983). Therefore, it is hypothesized that application rates of encapsulated formulations could be reduced because these potential losses to the environment no longer have to be compensated for. Furthermore, the recently reported detection of herbicides in rain (Glotfelty and others, 1987; Richards and others, 1987) could be reduced substantially as little or none of the herbicide would be lost to the atmosphere during spraying because the product would be applied as a dry granule.

To our knowledge, no field-dissipation studies that assess the release patterns of starch-encapsulated herbicides in the environment have been reported. The objective of this paper is to provide evidence that such a formulation can reduce the mass of herbicide washed from a field during surface runoff and thereby reduce herbicide loads in surface water, especially during the "spring flush" period immediately after herbicide application. It is hypothesized that, if encapsulated formulations released herbicides slowly into the soil, the mass available for washoff directly after application would be minimal. Previous studies of the chemistry of surface water (Wauchope, 1978; Glotfelty and others, 1984; Leonard, 1988) have shown that the first overland runoff after application of conventional powdered formulations has the greatest herbicide load and can introduce a substantial mass of active chemical into nearby water bodies. Eventually, this is reflected in increased herbicide concentrations in major rivers, such as the Mississippi River and its tributaries (Pereira and Rostad, 1990). Long-term storage of herbicide-laden water in reservoirs can have additional deleterious effects on aquatic vegetation (Butler and others, 1975; deNoyelles and others, 1982; Jones and Winchell, 1984; Kosinski and Morris, 1984). Furthermore, conventional water-treatment practices are unable to remove these soluble herbicides (Kearney and others, 1988; Miltner and others, 1989), and large concentrations could contaminate drinking water.

EXPERIMENTAL PROCEDURES

Field Study Area

The herbicide field-dissipation study was conducted at the Silver Lake Experimental Field Site, near Topeka, Kans. (fig 1). Two 45-square meter clayey-loam and sandy-loam plots, each with a slope of less than 1 percent,

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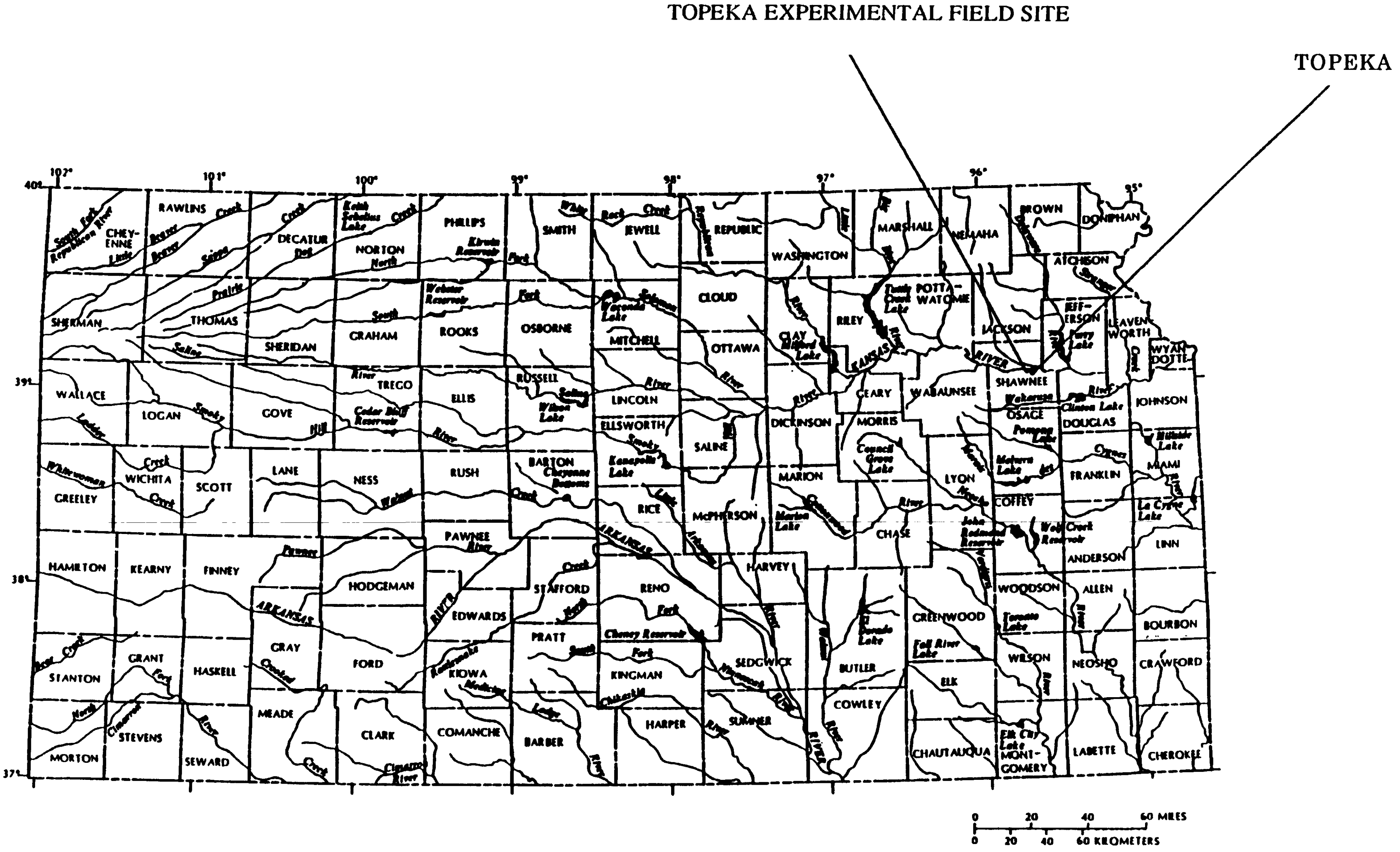
TOPEKA EXPERIMENTAL FIELD SITE
TOPEKA
102°
101°
100°
99°
98°
97°
96°
95°
40°
39°
38°
37°
CHEYENNE
RAWLINS
DECATUR
NORTON
PHILLIPS
SMITH
JEWELL
REPUBLIC
WASHINGTON
MARSHALL
NEMAHA
BROWN
DONIPHAN
SHERMAN
THOMAS
SHERIDAN
GRAHAM
ROOKS
OSBORNE
MITCHELL
CLOUD
CLAY
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POTTAWATOMIE
JACKSON
ATCHISON
JEFFERSON
LEAVENWORTH
WYANDOTTE
WALLACE
LOGAN
GOVE
TREGO
ELLIS
RUSSELL
LINCOLN
ELLSWORTH
OTTAWA
SALINE
DICKINSON
GEARY
MORRIS
WABAUNSEE
SHAWNEE
OSAGE
DOUGLAS
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ALLEN
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KIOWA
ELK
WILSON
NEOSHO
CRAWFORD
MORTON
STEVENS
SEWARD
MEADE
CLARK
COMANCHE
BARBER
HARPER
SUMNER
COWLEY
CHAUTAUQUA
MONTGOMERY
LABETTE
CHEROKEE
KANSAS RIVER
ARKANSAS RIVER
Cedar Bluff Reservoir
Kirwin Reservoir
Webster Reservoir
Wilson Lake
Kanopolis Lake
Waconda Lake
Tuttle Creek Lake
Milford Lake
Council Grove Lake
Marion Lake
Cheney Reservoir
El Dorado Lake
Fall River Lake
Toronto Lake
Elk City Lake
John Redmond Reservoir
Perry Lake
Clinton Lake
Pomona Lake
Melvern Lake
Hillsdale Lake
La Cygne Lake
Keith Sebelius Lake
Cheyenne Bottoms
0 20 40 60 MILES
0 20 40 60 KILOMETERS

Figure 1. Location of Topeka and Topeka Experimental Field Site in Kansas. Rivers and reservoirs of the State are also shown.

were equipped with a 380-L (liter) storage tank, a sump pump and hose, and a large sunken bucket. During a rainstorm or sprinkler applied irrigation, surface runoff was collected in the sunken bucket and pumped by the sump pump through the connecting hose into the large storage tank. Sump pumps were operated by a solar-powered battery. Each plot was isolated from the others by berms and flashing. Encapsulated atrazine and alachlor were applied simultaneously at a rate of 2 kilograms per hectare (active ingredient) to one plot by means of a calibrated fertilizer distributor, and the powdered formulation of atrazine and alachlor was applied at the same rate on the remaining plot by spraying. Each plot was covered by a large sheet of polyurethane plastic to protect it from herbicide drift during herbicide application on a nearby plot. The herbicides were incorporated into the soil to a depth of approximately 5 cm (centimeters) with a rotor tiller. A total of 42 cm of water was applied to each plot either by natural precipitation or a sprinkler irrigation system. The entire volume of water running off each plot was collected in the large storage tank, to determine total mass of herbicide. A 4-L sample of water was collected from each storage tank for analysis. Runoff from each plot was collected during a 72-day period, after which the plots were allowed to dry so that corn could grow and ripen. This was followed by ploughing and mixing the soil with corn stalks and detritus remaining on the field. The dry and blocky nature of the soil, mixed with the corn detritus, increased the moisture infiltration capacity of the soil so that no further runoff took place.

Methanol, ethyl acetate, and isooctane were used as pesticide grade solvents. Deionized water was charcoal-filtered and glass-distilled prior to use. Atrazine, terbuthylazine, alachlor and the triazine metabolites, deethylatrazine and deisopropylatrazine, were obtained from various sources for use as standards in the study. Solid-phase C_{18} Sep-Pak[4] cartridges contained 360 milligrams of 40-micrometers C_{18}-bonded silica. Standard solutions were prepared in methanol, and d-10 phenanthrene was used as an internal gas chromatography/mass spectrometry (GC/MS) quantitative standard.

Solid Phase Extraction Procedure

A Waters Millilab Workstation was used for solid-phase extraction of the analytes. Cartridges were preconditioned sequentially with methanol, ethyl acetate, methanol, and distilled water (3 mL (milliliters) of each).

Each water sample was spiked with a surrogate standard, terbuthylazine, and passed through the cartridge at a rate of 20 milliliters per minute. The analytes were eluted with 4 mL of ethyl acetate and spiked robotically with deuterated phenanthrene. The ethyl acetate layer was transferred from a small co-eluted water layer, to a centrifuge tube, for automated evaporation at 45 °C (degrees Celsius) under a nitrogen stream to 100 microliters.

GC/MS Analysis

Automated GC/MS analyses of the eluates were performed under conditions according to Thurman and others (1990).

RESULTS AND DISCUSSION

The release patterns of the encapsulated and powdered formulations of atrazine and alachlor into runoff waters are shown in figure 2. Volumes of runoff water and concentrations of herbicide for each period of runoff are listed in table 1. As hypothesized, the first runoff sample after application of the encapsulated herbicides contained a small mass of herbicide because only a small quantity was present in its soluble form on the field. With time, the mass available for washoff from the encapsulated plot increased, as the herbicides were slowly released from the protective starch-matrix, and the distribution of mass throughout the growing season followed a normal-distribution-shaped curve. However, the first runoff sample from the powdered herbicides had a high mass present, and in subsequent runoff through time this decreased in an exponential manner. Twenty times more mass was washed from the powdered-herbicide plot than from the encapsulated-herbicide-plot during the first runoff after application. Throughout the entire runoff season, approximately 30 percent more herbicide mass was washed from the powdered herbicide plot into nearby water bodies than from the encapsulated-herbicide plot.

The significant difference in the patterns of herbicide runoff can be explained by examining the nature of the encapsulated herbicide formulation. The starch-encapsulating matrix is depicted in figure 3 as chains of glucose units linked as both straight (amylose) and branched (amylopectin) chains. Herbicide molecules are trapped between the chains, and the degree of encapsulation is a function of the ratio of amylose to amylopectin. Amylose concentrations that exceed approximately 20 percent lock together the matrix so tightly that less herbicide is trapped, and the herbicide that is present is less able to escape. Too little amylose, however, creates an open matrix, which allows water molecules to invade the structure and solubilize the herbicides too rapidly. With an optimum of 10 percent amylose, water molecules can infiltrate slowly and solubilize the herbicide. Biodegradation of the matrix also may occur simultaneously, and, in this way, the herbicide is slowly released. Conversely, the initially large powdered herbicide peak results from the large mass of soluble herbicide present immediately after application. This mass decreases exponentially through time as the remaining herbicide is lost through leaching, volatilization, plant uptake, and degradation.

Encapsulated herbicide release characteristics in solution with distilled water and methanol show the rapidity of herbicide release (table 2). In aqueous solution, the starch swells to such an extent that all of the herbicide escapes. These aqueous release characteristics indicate that, should the starch granule be washed off a field along with suspended sediments, all herbicide from the granule will enter the aqueous phase rapidly, increasing herbicide concentrations. Table 2 also documents the more rapid release of alachlor over a 48-hour period from the starch-encapsulating matrix compared to atrazine. This pattern is

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[4] The use of trade names is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

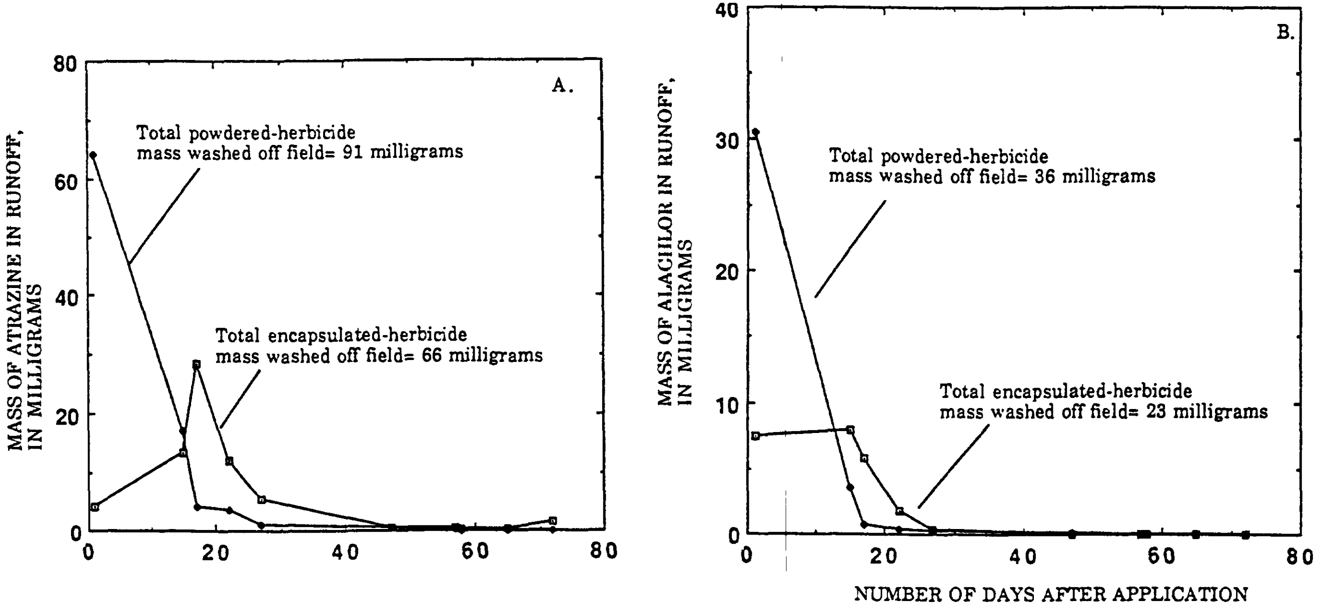

Figure 2. Mass of (A) atrazine and (B) alachlor in runoff from a silt-loam plot after application of powdered- and encapsulated-herbicide formulations.

also reproduced in the field experiment (fig 1), where two times as much alachlor is released from the starch matrix in the first runoff sample compared to atrazine. This indicates that the greater solubility of alachlor renders it less protectively encapsulated within the starch matrix as compared to atrazine.

Atrazine metabolites present in runoff from both powdered- and encapsulated-herbicide plots are shown in figure 4. Deethylatrazine is the major degradation product from both plots, and its appearance, along with deisopropylatrazine, is similar to the parent compound, atrazine. The quantity of degradation products present from the powdered formulation is initially greater than that from the encapsulated product. With time, however, metabolite concentration in the encapsulated-herbicide plot increases, as more of the parent herbicide is released from the starch matrix.

The ratio of degradation products to parent atrazine remains almost constant throughout their appearance, indicating that their production depends on the mass of atrazine present. The ratio of deethylatrazine to deisopropylatrazine remains almost constant at approximately 3:1, and the ratio of atrazine to deethylatrazine remains at approximately 100:1.

Table 1. *Volume of runoff and concentrations of parent herbicides from each experimental plot during runoff season*

Days after application	Volume of runoff (liters)	Rainfall (centimeters)	Concentration of herbicide or metabolite, in micrograms per liter			
			Alachlor	Atrazine	Deethylatrazine	Deisopropylatrazine
				Encapsulated formulation		
1	380	5	19.6	11.4	0.3	0.06
15	380	5	21	35.2	.05	.05
17	938	2.5	6.2	30.5	.05	.05
22	100	4	4.7	32	2.5	.63
27	380	3	1	14.5	.48	.02
57	23	7.5	1.7	20.5	1.3	0.5
58	38	2.5	1.2	9.3	.12	.05
65	23	.4	6	.4	.2	
72	304	.04	5	.4	.2	
				Powdered formulation		
1	1,520	5	20	42.2	1.4	.6
15	380	5	9.2	45.1	1	0
17	395	2.5	1.7	10.6	.4	.05
22	380	4	1.0	10	1.4	.4
27	380	3	.4	2.7	.05	..05
47	38	5	2.3	12.6	1	.2
57	231	7.5	.2	1.2	.05	.2
58	30	2.5	.3	1.3	.05	.05
65	92	.4	.003	.7	.25	.12
72	304	.04	.04	.22	.1	.04

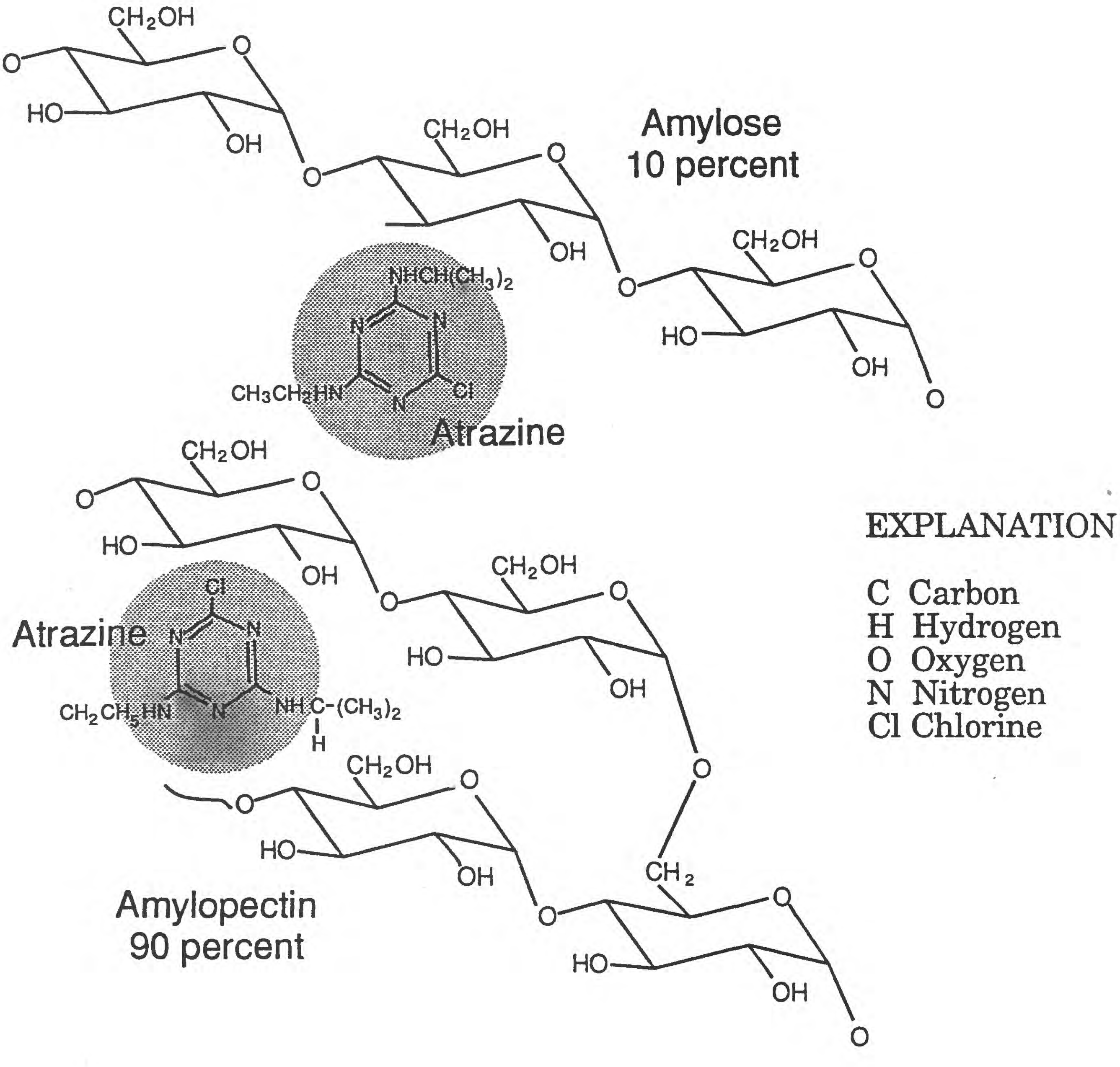
Amylose
10 percent
Atrazine
Atrazine
Amylopectin
90 percent
CH₂OH
HO
OH
O
CH₂
NHCH(CH₃)₂
CH₃CH₂HN
N
Cl
NH C-(CH₃)₂
H
CH₂CH₂HN
EXPLANATION
C Carbon
H Hydrogen
O Oxygen
N Nitrogen
Cl Chlorine

Figure 3. Diagram showing conceptual starch matrix encapsulating atrazine molecules.

Table 2. *Release characteristics over time of encapsulated atrazine and alachlor in methanol and water solutions at 25 and 75 degrees Celsius*

	Percent (± 5 percent) of herbicide released				
Time (hours)	Water 25 °C	Water 75 °C	Methanol 25 °C	Methanol 75 °C	Water and methanol 75 °C
			Atrazine		
1	2.6	36.4	6.4	25.2	67
24	7.4	34.6	10.2	32.6	73.2
48	12.8	39.2	13.6	46	86.4
			Alachlor		
1	16.4	72.2	12.8	43.2	91
24	45.4	79.8	69.8	55.6	87.8
48	76.6	100	79.8	74.4	100

CONCLUSIONS

1. Encapsulated herbicides can decrease the mass of herbicide entering surface-water bodies in runoff water by approximately 30 percent compared to powdered formulations.
2. Encapsulated herbicides can reduce the initial flush of large concentrations of herbicides from a field immediately after application by a factor of approximately 20. This reduction would eliminate the pulse of herbicides presently documented to move through streams immediately following application and cause drinking-water regulations for surface water to be exceeded (E.M. Thurman and others, U.S. Geological Survey, written commun., 1991). Use of encapsulated herbicides would produce a more uniform flux of herbicides that enter water bodies over time and would enhance the effectiveness of dilution.
3. Application rates of encapsulated herbicide formulations could be reduced according to soil type because no compensation is needed for losses by volatilization during spray application and from the field surface, by surface runoff, or by downward leaching of the herbicides.
4. Use of encapsulated-herbicides in a watershed could improve the quality of surface water in the area by decreasing the rate of release into runoff.
5. Encapsulated herbicides, applied as a solid granule, may reduce the presence of herbicides in rain by eliminating problems of drift during spray application and field-surface volatilization.

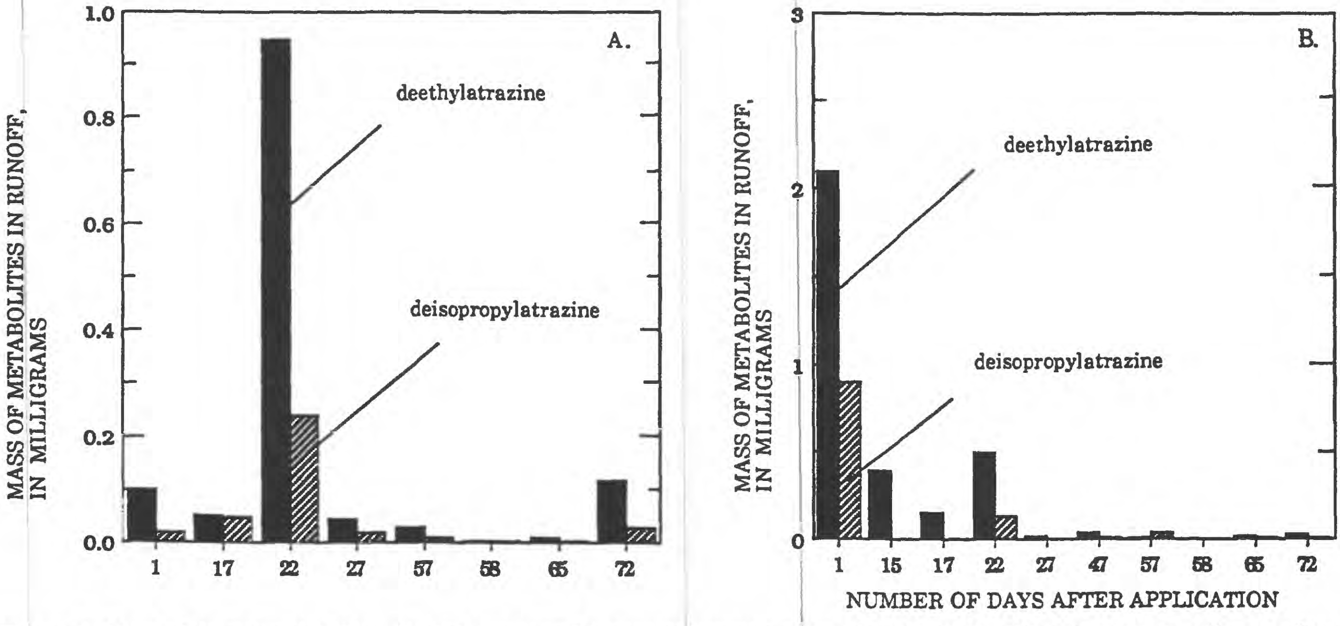

Figure 4. Mass of atrazine metabolites, deethylatrazine and deisopropylatrazine, present in runoff waters throughout the runoff season from (A) encapsulated- and (B) powdered herbicide plots.

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SPATIAL VARIABILITY IN HYDRAULIC CONDUCTIVITY OF A SILT-LOAM SOIL NEAR TOPEKA, KANSAS

By David A. V. Eckhardt[1] *and* Philip L. Barnes[2]

ABSTRACT

A soil's hydraulic conductivity can be estimated fairly accurately from undisturbed profiles under conditions of steady-state ponded infiltration by monitoring the drainage and redistribution of soil water in the profile after cessation of infiltration. An exponential relation of unsaturated soil hydraulic conductivity [$K(\theta)$] to water content (θ) is assumed in the form of

$$K(\theta) = K_o \,.\, \exp\,[\beta(\theta - \theta_o)\,]\;,$$

where

K_o *is the hydraulic conductivity during steady-state ponded infiltration,*
θ_o *is the corresponding soil-water content during steady-state ponded infiltration, and*
β *is a dimension less constant.*

In this study, the spatial distributions of β and K_o at selected depths were determined by measurements of soil-water content after the cessation of infiltration (θ_o - θ) over time at each of 8 depths at 18 locations in a 0.75- hectare silt-loam plot near Topeka, Kansas. Values of β and K_o for 133 of the measurements were approximately log-normally distributed about their means. Mean β was 74, and mean K_o was 0.12 centimeters per hour. The values of K_o and β measured at one site were used in a numerical unsaturated flow model to simulate decreasing water content in the soil profile during drainage. Model results indicate that the field method provides reasonable estimates of K_o and β and that simplifying assumptions were accurately met. Differences between simulated and measured water contents in the selected soil profile are attributed to vertical variability in other soil physical properties, such as moisture-retention characteristics and bulk density, which would need to be quantified spatially to improve simulation.

INTRODUCTION

Soil properties have inherent nonuniformity that affects the spatial distribution of soil-water content and movement. Water movement within the soil profile largely controls the movement and fate of dissolved chemicals and their potential for subsurface leaching to ground water. The spatial variability of soil properties over substantial land areas must be considered when making estimates of solute concentration and soil-water velocity. Soil properties of interest include hydraulic conductivity, soil-water content, bulk density, organic-carbon content, texture, and moisture retention characteristics. The problem addressed in this study was to evaluate the spatial variability of the hydraulic conductivity of an unsaturated silt-loam soil.

Hydraulic conductivity of soils is best estimated in the field on undisturbed profiles. Relatively accurate results can be obtained for conditions of steady-state infiltration of artificially ponded water followed by monitoring the redistribution and drainage of soil water in the profile after cessation of infiltration, which allows determination of the hydraulic conductivity during ponded steady-state infiltration (K_o) and the hydraulic conductivity $K(\theta)$ as a function of soil-water content (θ) at differing soil depths and locations. The statistical distributions of these and other properties can then provide a basis for evaluating spatial variability in soil-water and chemical movement.

In June 1990, the U.S. Geological Survey began a study to characterize field- scale spatial variability of K_o and $K(\theta)$ and relate these properties to observed vertical movement of soil water. Data collection was limited to the top 120 cm (centimeters) of a 0.75-ha (hectare) silt-loam soil agronomic plot in a flood-plain setting at the 32-ha Kansas River Valley Experiment Field near Topeka, Kans. Hydraulic conductivity was measured at 8 depths (15-cm vertical separation) at each of 18 locations within the plot (fig. 1). Locations of a ground-water monitoring well and four excavation pits for core sampling for moisture retention characteristics also are shown in figure 1, but discussion of these is beyond the scope of this paper. A typical vertical profile at the site consisted of 1.2 m (meter) of fairly uniform silt loam over a 1.8-m transition zone of layered silty, clayey, and sandy loam, which overlies about 3 m of medium to coarse alluvial sand. The water table is in the alluvial sand about 6 m below land surface. Crops are typically rotated annually between corn and soybeans, but a cover of alfalfa was used during this 6-month study.

This paper describes a simple field method for determining hydraulic conductivity of an unsaturated soil profile and presents a statistical summary of measurements at 133 locations within the 0.75-ha silt-loam plot. A simulation of decreasing water content after cessation of infiltration in one soil profile is presented to evaluate the use of the method at the field site.

METHODS

Eighteen aluminum neutron access tubes (5-cm diameter) were installed to 6-m depths at 10 locations and to 3-m depths at 8 locations in a 15-m grid pattern (fig. 1). At each tube location, K_o and β were measured at 15-cm depth intervals through unit-gradient ponded infiltration and drainage methods described and evaluated by Libardi and others (1980), Sisson and others (1980), and Jones and Wagenet (1984). The method entails ponding water at a constant head within 100-cm diameter steel rings sealed 15 cm into the soil around each access tube. Water infiltrates until steady-state flow is observed through stabilized neutron-probe measurements of water content throughout the soil profile to the 120-cm depth. Infiltration is then discontinued, the ring is removed, and plastic sheeting is installed around the tube to prevent evaporation from or infiltration of rainfall into the plot during redistribution and drainage. Water content is measured with a neutron probe at each 15-cm depth interval from the surface to the 120-cm depth during a period of up to 16 days after drainage begins. The theory of the method is based on the Richards' equation for describing unsaturated flow:

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$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z}\left[\frac{K(\theta)\cdot \partial h}{\partial z}\right] \qquad (1)$$

where

θ is volumetric water content, in cubic centimeters of water per cubic centimeter of soil;
t is time (hours);
K is hydraulic conductivity, in centimeters per hour;
h is total hydraulic head, in centimeters, composed of the sum of matric (pressure) and gravitational heads; and
z is soil depth, in centimeters.

The following assumptions inherent in the unit-gradient method are described by Jones and Wagenet (1984). $K(\theta)$ is expressed as

$$K(\theta) = K_o \cdot \exp\left[\beta(\theta - \theta_o)\right], \qquad (2)$$

where

β is a constant at each depth, and
K_o and θ_o are the values of K and θ at each depth during steady-state infiltration.

At the start of the test, immediately after ponding is ended, soil-water flux is assumed constant at all depths in the measured profile (steady-state). A unit hydraulic gradient is assumed to cause soil-water movement during redistribution and drainage; that is,

$$\frac{\partial h}{\partial z} = -1. \qquad (3)$$

To express this explicitly, the average soil-water content (θ^*) from the surface to depth z can be related to the soil-water content (θ) measured at depth z by the following linear relation;

$$\theta^* = a\,\theta + b, \qquad (4)$$

where a and b are regression slope and intercept values.

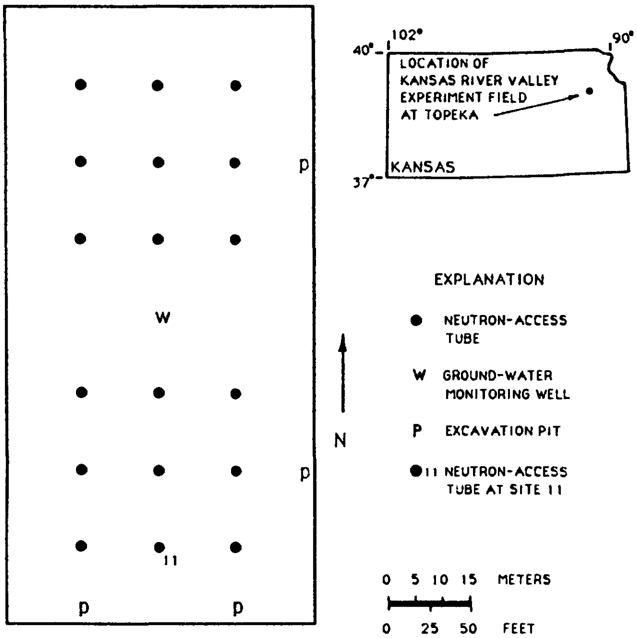
From equations (1-4), the following expression is presented by Libardi and others (1980):

$$\theta_o - \theta = \frac{1}{\beta}\ln(t) + \frac{1}{\beta}\ln\left[\frac{\beta K_o}{a z}\right]. \qquad (5)$$

This relation indicates that, at any depth, the change in water content from its wettest condition ($\theta_o - \theta$) to some time (t) is linearly related to ln(t). Thus β is the reciprocal of the slope of the linear relation and K_o is determined from the intercept term (Y_{int}) in equation 5 by simple regression, where

$$K_o = \frac{a z}{\beta}\exp\left[\beta Y_{int}\right]. \qquad (6)$$

The values of β and K_o needed to define $K(\theta)$ by equation (2) may therefore be determined by the appropriate measurements of $\theta_o - \theta$ over time for each of 8 depths at 18 locations within the plot.


102°
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LOCATION OF KANSAS RIVER VALLEY EXPERIMENT FIELD AT TOPEKA
KANSAS
W
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EXPLANATION
● NEUTRON-ACCESS TUBE
W GROUND-WATER MONITORING WELL
P EXCAVATION PIT
●11 NEUTRON-ACCESS TUBE AT SITE 11
0 5 10 15 METERS
0 25 50 FEET

Figure 1. Location of Kansas River Valley Experiment Field and neutron access tubes at the field plot.

RESULTS AND DISCUSSION

Values of β and K_o were determined at 144 locations within the plot. A sample graph showing the decline in water content through time at two depths at site 11 is shown in figure 2A. Plots of change in water content over natural-log time showing β and K_o values determined by equations 5 and 6 from the simple linear regression lines fitted by equation 5 for the same two depths are shown in figure 2B. Several shallow depth zones were affected by influx of water from rainfall that leaked into the subsurface around the access tube during the test. These measurements were discarded from further analysis because determination of β and K_o at these locations was impossible. For the remaining 133 sets of drainage data, the median r^2 (coefficient of determination) was 0.95. The relatively good fit in regression lines, shown by high r^2 and low standard errors of estimate, indicates that the method is applicable to this soil and that K_o and β were estimated with acceptable accuracy.

Fractile diagrams showing the cumulative probability distributions of K_o and β for the 133 measurements are shown in figures 3A and 3B. The values of both K_o and β for all depths combined are approximately log-normally

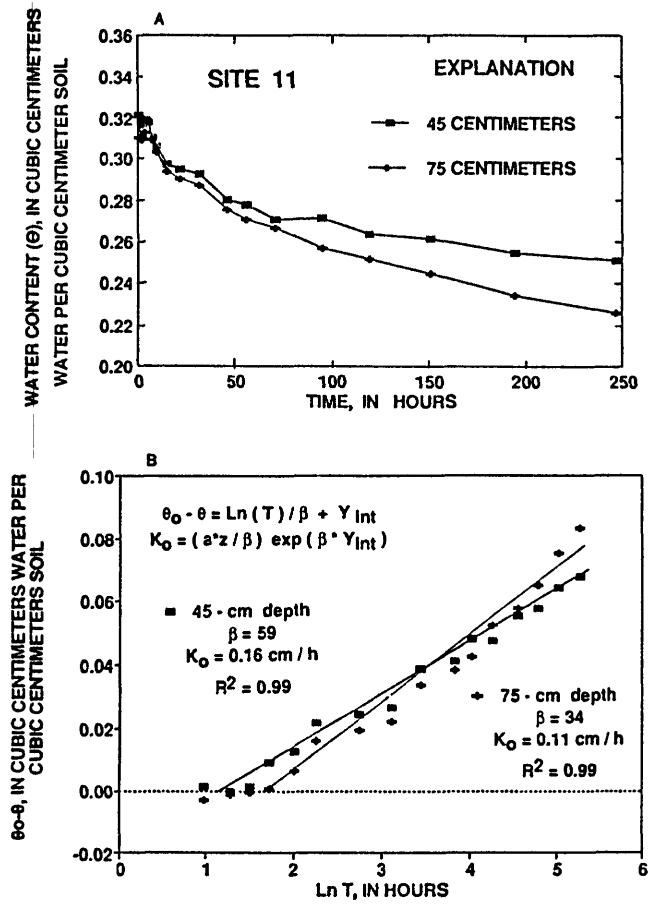

Figure 2. Drainage curve for 45-centimeter and 75-centimeter depths at site 11 expressed as (A) water content over time, and (B) change in water content over ln (time) showing fitted regression lines (K_o in centimeter per hour and β dimensionless.)

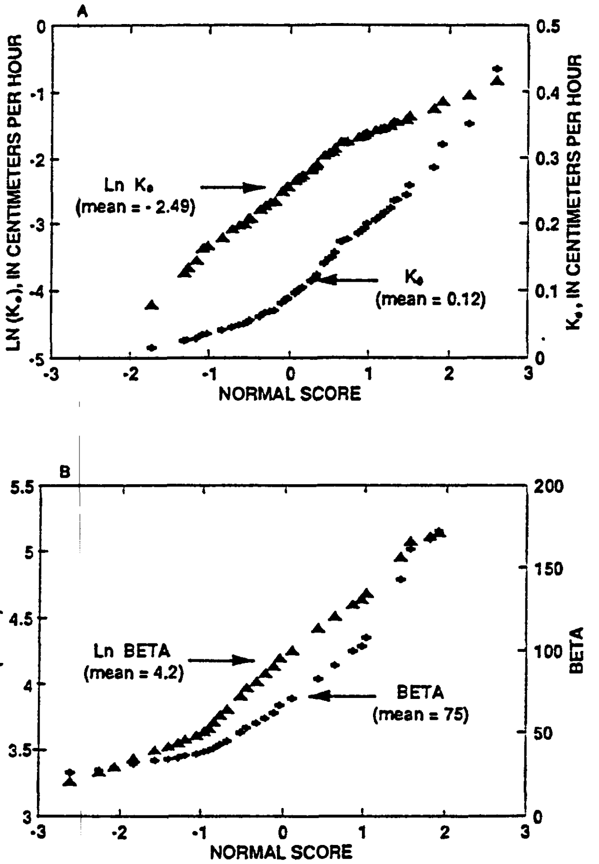

Figure 3. Cumulative probability plots of the distribution of (A) K_o and (B) β.

Table 1. *Means and variances computed for log-normal distributions of Ko and β by 18 locations.*

[K_o in centimeters per hour and β dimensionless.]

Depth (cm)	n^1	K_o Mean (cm/h)	K_o Variance (cm^2/h^2)	β Mean	β Variance
15	15	0.046	0.0019	62	460
30	14	.067	.0046	81	2,217
45	16	.11	.013	93	3,824
60	16	.11	.0065	76	2,285
75	18	.12	.0070	66	1,086
90	18	.12	.0063	69	758
105	18	.17	.026	75	890
120	18	.18	.026	86	3,030
$0\text{-}120^2$	133	.12	.015	74	1,503

[1] Number of measurement locations

[2] All depths combined

distributed about their means. Log-normal distributions of K_o and β by depth and for all depths combined have been observed in other soils, such as a clayey loam (Nielsen and others, 1973) and a sandy loam (Jones and Wagenet, 1984). Estimates of the means and variances of K_o and β are calculated from an assumed log-normal distribution for all values combined and for each depth (table 1). An increase in mean K_o as depth increases is observed, whereas no changes in β with depth are observed.

The measured values of K_o and β were used with equations 1 and 2 in a numerical simulation of soil-water redistribution and drainage at access-tube site 11 to see how well simulated water contents matched actual field measurements. The numerical model used was LEACHP (Wagenet and Hutson, 1989), which simulates the transient-state one- dimensional movement of soil water and dissolved pesticides. Measured values of K_o and β were assigned to 15-cm thick model layers, and initial conditions were set to observed water content (θ_o) at the end of steady-state ponded infiltration. The simulated and observed water contents 2 days and 10 days after drainage began within the 120-cm soil profile are compared in figure 4. The simulated and observed values are within 5 percent of one another at the 15, 60, 75, and 120-cm depths, but the simulated values are 6 to 18 percent less than observed values at the other four depths. The differences probably are due, in part, to use of uniform soil-moisture retention characteristics for all depths, when the retention characteristics (and bulk density) probably vary with depth, as indicated by the nonuniformity in initial water contents

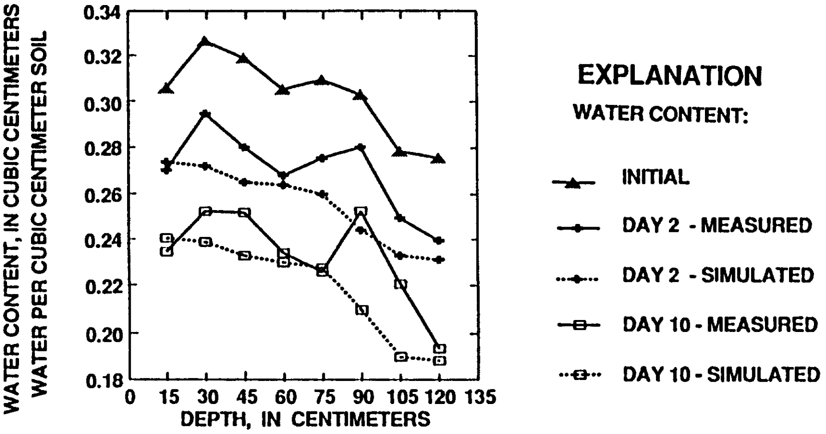

Figure 4. Comparison of observed and simulated water content 2 days and 10 days after cessation of infiltration based on on the β and K_o vertical distribution measured at site 11.

and variable β and K_o for each layer. The general agreement between transient-state simulated and observed water contents at this location indicates, however, that the measurements of K_o and β by the unit-gradient method at the Topeka site are reasonably accurate. Continuing work in measuring the vertical variability of other soil properties, such as bulk density and moisture-retention characteristics (relation of pressure-head to water content) is expected to provide additional information needed to accurately model soil water and chemical movement within the silt-loam plot.

SUMMARY AND CONCLUSIONS

A relatively simple field method was used to determine the variability in saturated and unsaturated hydraulic conductivity of a 120-cm deep horizon of a silt-loam soil. The method uses the Richards' equation for transient-state unsaturated flow and an exponential representation of hydraulic conductivity as a function of water content. The method was used to characterize soil hydraulic conductivity (K_o) under steady-state infiltration ponded infiltration and the slope (β) of the exponential relation of unsaturated hydraulic conductivity to water content at 8 depths at 18 locations at a field site near Topeka, Kans. Values for K_o and β were determined at 133 locations within a 0.75-ha plot for which the physical assumptions of the method applied.

The values of both K_o and β were approximately log-normally distributed about their means when data were combined for all depths. Mean K_o was 0.12 centimeter per hour and mean β was 75. The mean K_o increases as depth increases, but no change in β by depth was observed. Simulations of decreasing water content in the soil profile after cessation of infiltration at one site indicates that the field method provides reasonable estimates of K_o and β and that method assumptions have been adequately met. Differences in simulated and measured water contents in the selected soil profile are attributed to vertical variability in other soil physical properties, such as moisture-retention characteristics and bulk density, which must also be determined spatially. Continuing work in measuring the vertical variability of these and other soil properties is expected to provide additional information needed to accurately describe soil water and chemical movement within the silt-loam plot.

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INTEGRATED HYDROLOGIC RESEARCH AT THE NORTHERN CORN BELT SAND-PLAIN MANAGEMENT SYSTEM EVALUATION AREA, MINNESOTA

By Geoffrey N. Delin[1], James L. Anderson[2], and Robert H. Dowdy[3]

ABSTRACT

The U.S. Geological Survey, in cooperation with the U.S. Department of Agriculture and the U.S. Environmental Protection Agency, is conducting interdisciplinary research on the effects of agricultural practices on water quality. A 0.65 square-kilometer site located near the town of Princeton, Minnesota, was selected for intensive research in the Anoka sand-plain aquifer to represent hydrogeologic conditions typical of the Midwest corn belt sand plains. The site is adjacent to and upgradient from a stream and associated wetland. Material in the unsaturated and saturated zones at the site generally consists of fine-to-medium sand and medium-to-coarse sand, respectively. The saturated thickness of the aquifer is about 8 meters. The water table is from 0 to about 3 meters below land surface. The estimated horizontal hydraulic conductivity is about 10 centimeters per day.

The overall approach to conducting research at the Northern Corn Belt Sand-Plain Management System Evaluation Area is to identify and evaluate important processes and factors affecting the behavior and fate of agricultural chemicals in the environment. Multidisciplinary, multiscale research is planned for selected transport, transformation, and phase-transfer processes affecting the fate of agricultural chemicals in the various environmental compartments (atmosphere, soil/root zone, unsaturated zone, saturated zone, and surface water). The U.S. Geological Survey Minnesota District will be coordinating physical and chemical hydrologic research and will provide logistical support for Survey and U.S. Environmental Protection Agency researchers at the Princeton site.

INTRODUCTION

Nonpoint-source contamination of surface and ground water by agricultural chemicals is a problem of increasing environmental concern. The midcontinental region of the United States is considered one of the principal areas susceptible to nonpoint-source contamination of ground and surface waters because the region is dominated by cropland, primarily corn and soybean production, where applications of pesticides and fertilizers are substantial (Burkart and others, 1988). The U.S. Geological Survey (USGS), in cooperation with the U.S. Department of Agriculture (USDA) and the U.S. Environmental Protection Agency (USEPA), is proposing interdisciplinary research on the effects of agricultural practices on water quality at five representative sites in the Midwest corn belt. These Management System Evaluation Areas (MSEA) were implemented under the research component of the President's Water Quality Initiative. This interagency initiative resulted from merging the USDA's Research Plan for Water Quality with the USGS's Midcontinent Herbicide Initiative (Burkart and others, 1988). The overall objectives of the research program are to (1) evaluate the impact of agricultural practices on water quality, and (2) develop new and improved agricultural systems to reduce the movement of agricultural chemicals, particularly atrazine and nitrate, to water resources.

The purpose of this paper is to describe (1) the hydrogeologic setting of the Northern Corn Belt Sand-Plain MSEA, (2) the proposed agricultural practices, (3) the Minnesota core project that supports research activities, and (4) the interdisciplinary research plan for the Northern Corn Belt Sand-Plain MSEA.

HYDROGEOLOGIC SETTING

The Northern Corn Belt Sand-Plain MSEA is typified by flat-lying surficial glacial deposits, or sand-plain aquifers. These aquifers represent an area of the Midwest corn belt that is susceptible to ground-water contamination by land application of agricultural chemicals (Klaseus and others, 1988). Sand-plain aquifers are hydrogeologically vulnerable because they are characterized by extreme values in many of the hydrogeologic factors affecting the fate and transport of agricultural chemicals, such as high hydraulic conductivity (in soil and unsaturated and saturated zones), shallow depth to the water table (Lindholm, 1980), flat topography and low runoff, high rates of recharge and ground-water seepage velocity, high base flow or seepage to surface-water bodies, and low organic carbon.

The principal research site is near Princeton, Minn., within the 4,400-km^2 (square kilometer) Anoka sand-plain aquifer. Satellite sites are on outwash plains in North Dakota, South Dakota, and Wisconsin (fig. 1). The Anoka sand plain is an area of glacial outwash along the Mississippi River. Previous investigations have documented that the aquifer is susceptible to contamination from agricultural chemicals (Lindholm, 1980; Anderson, 1989; Anderson and Stoner, 1989). The 0.65-km^2 research site is in Sherburne County about 80 km (kilometers) northwest of Minneapolis and St. Paul (fig. 1). Results of corehole drilling at the Princeton site indicate that material in the unsaturated and saturated zones generally consists of fine-to-medium sand and medium-to-coarse sand, respectively. A 5- to 35-cm (centimeter) thick silty layer was identified within the unsaturated zone at six of the eight core-holes, at a depth of between 1.2 and 2.7 m (meters) below land surface. Results of augering in the middle of the field indicate that the silty zone is not present everywhere. The saturated thickness of the aquifer is about 8 m; with the water table being from zero to about 3 m below land surface. The estimated horizontal hydraulic conductivity is about 10 cm per day, and the estimated rate of ground-water recharge is about 20 cm per year.

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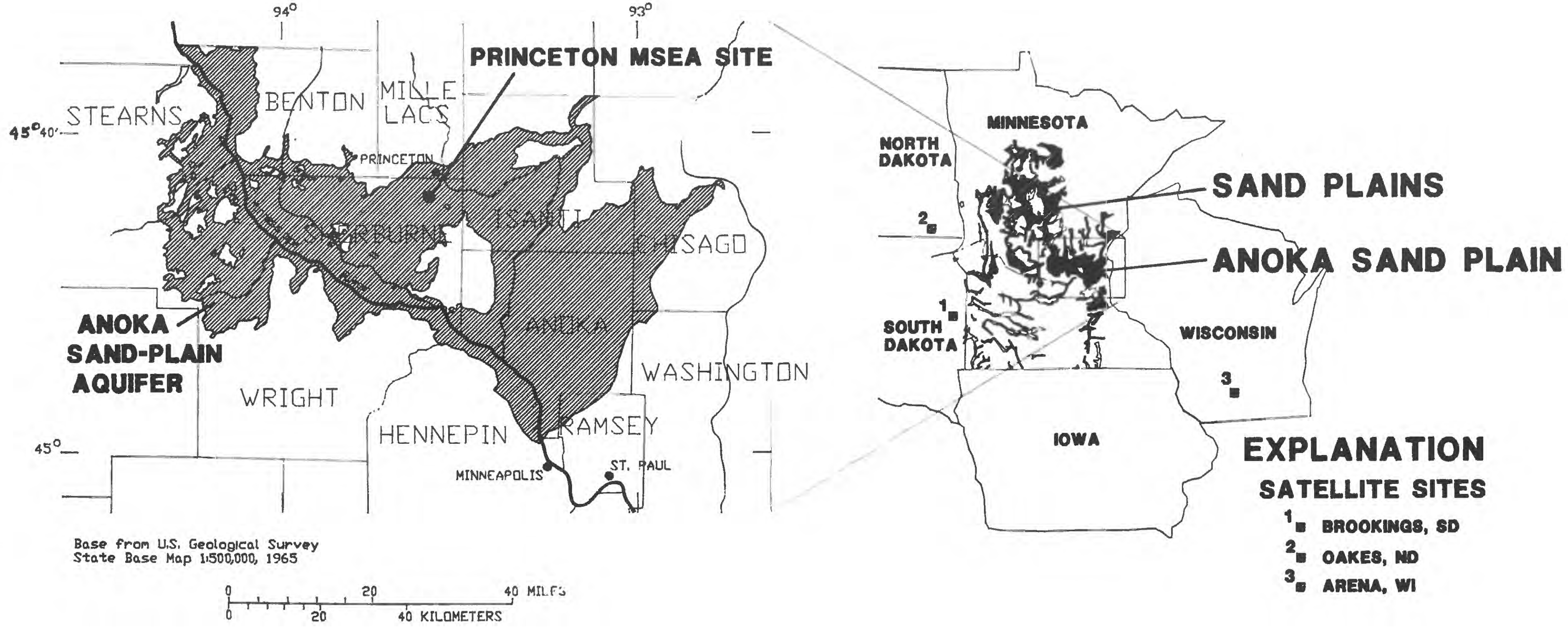

94°
93°
45°40′
45°
PRINCETON MSEA SITE
STEARNS
BENTON
MILLE LACS
PRINCETON
SHERBURNE
ISANTI
CHISAGO
ANOKA
ANOKA SAND-PLAIN AQUIFER
WRIGHT
HENNEPIN
RAMSEY
WASHINGTON
MINNEAPOLIS
ST. PAUL
0 20 40 MILES
0 20 40 KILOMETERS
MINNESOTA
NORTH DAKOTA
SOUTH DAKOTA
WISCONSIN
IOWA
SAND PLAINS
ANOKA SAND PLAIN
EXPLANATION
SATELLITE SITES
1 BROOKINGS, SD
2 OAKES, ND
3 ARENA, WI

Base from U.S. Geological Survey State Base Map 1:500,000, 1965

Figure 1. Northern Corn Belt Sand-Plain Management System Evaluation Area (MSEA).

Surface and ground waters are predominantly calcium bicarbonate types at the Princeton site. Ground-water samples were collected in October 1990 from two wells installed on the upgradient (western) side of the site (fig. 2). Field specific conductance was about 300 microsiemens per centimeter at 25 degrees Celsius. Based on results of immunoassay tests, triazine herbicides are not present in ground water at the site.

The Princeton site is favorable for conducting research on the fate and transport of agricultural chemicals for several reasons, in addition to the favorable hydrogeologic factors mentioned above: (1) A stream, Battle Brook, and an associated wetland in the northeastern corner of the site (fig. 2), will facilitate interdisciplinary research on the effects of agricultural practices on surface water quality--the stream forms natural hydrologic boundaries around the site; (2) previous use of agricultural chemicals upgradient from the site was minimal, in part because the Sherburne National Wildlife Refuge is located about 2.4 km to the west; (3) the Mount Simon-Hinckley aquifer, a confined bedrock aquifer isolated hydraulically from the surficial-sand aquifer by a 9-m-thick glacial-till confining unit, will supply irrigation water for the site with a minimum of hydraulic interference to the surficial aquifer; and (4) researchers may be able to use water from the Mount Simon-Hinckley aquifer as a tracer because its chemical composition differs from that of the water from the surficial aquifer.

PROPOSED AGRICULTURAL PRACTICES

The focus of USDA research at the Princeton site is to develop and evaluate farming systems designed to reduce the effects of agricultural chemicals on ground-water quality. This farming system will feature conservation (ridge) tillage and controlled application of water and agricultural chemicals. Two farming systems will be evaluated: field corn/soybean rotation and sweet corn/potato rotation (Anderson and others, 1991). Corn will be planted at the USGS recharge research site during each year of the study. The fields will be irrigated with water from an irrigation well completed in the underlying Mount Simon-Hinckley aquifer. Nitrogen-fertilizer and waterapplication rates will be scheduled to optimize crop production and minimize leaching of agricultural chemicals to ground water.

Four plots will be installed for the two cropping systems. Each plot is about 1.6 ha (hectares) per crop type (fig. 2). The plots will be oriented parallel to ground-water flow to minimize mixing of agricultural chemicals in the aquifer downgradient from the plots. A regional scale of study is incorporated into this study design by inclusion of satellite sites (fig. 1). Results of research in different climatic settings can be compared to reach regional conclusions.

CORE PROJECT

Specific objectives of the USGS core project in support of research activities at the Princeton site are to (1) describe the general hydrology and water quality at the principal research site near Princeton; (2) coordinate research activities and provide logistical support for USGS and USEPA researchers; (3) collect and report hydrologic and chemical data of common interest to participating scientists; and (4) quantify the concentrations of agricultural chemicals and their degradation products, spatially and in time, downgradient from the research plots.

Wetting fronts will be tracked through the unsaturated zone at the USGS recharge research site with the aid of ground-penetrating radar, time-domain reflectometry, thermocouples, and water and vapor probes. Suction lysimeters, soil-moisture blocks, and wick samplers will be used to sample water passing through the unsaturated zone.

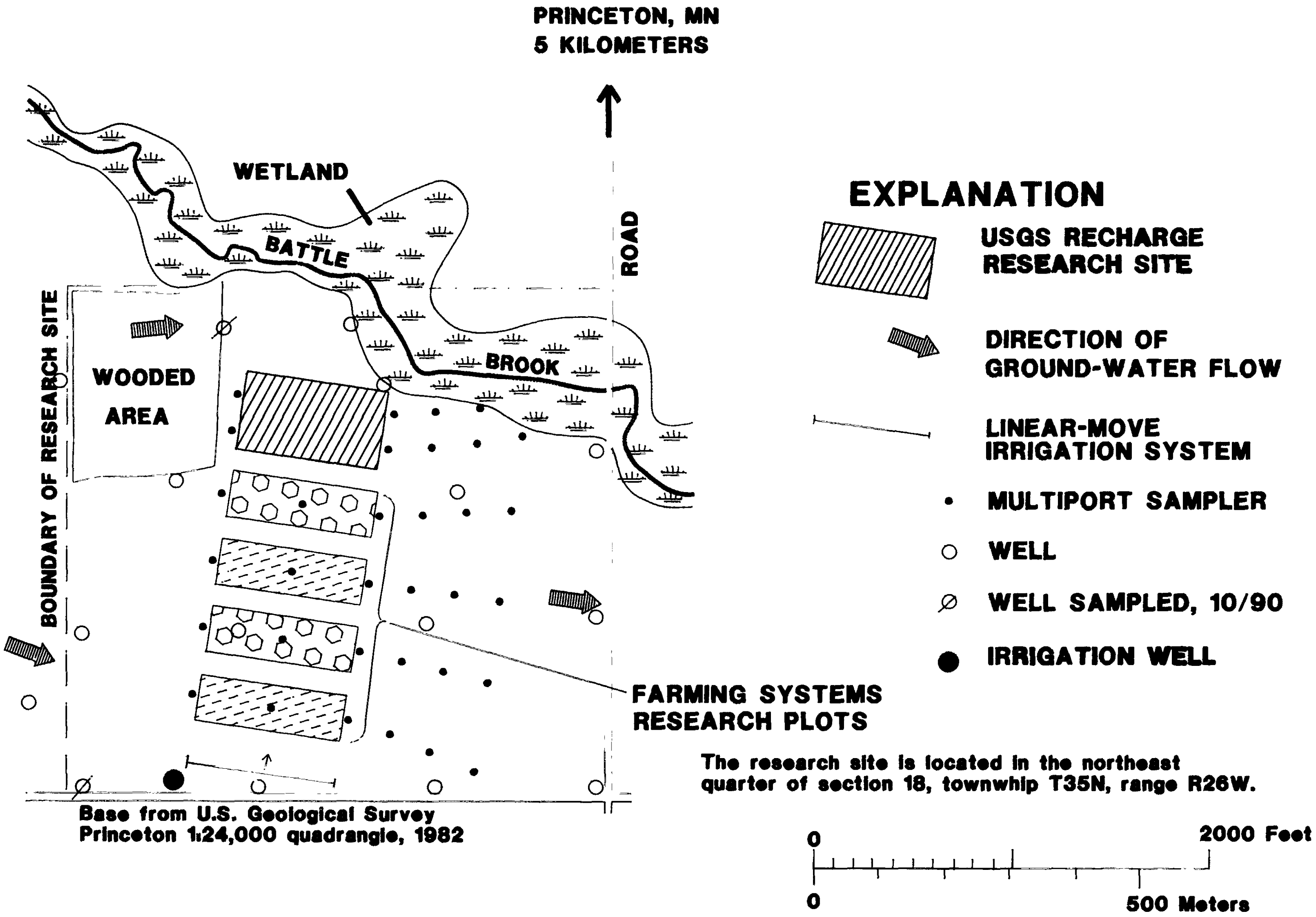
Multiport samplers and nests of observation wells will be installed in the saturated zone downgradient from the USGS recharge research site and the plots (fig. 2), and in areas where the silty zone is both present and absent, over the first 2 years of the study. The multiport sampling device will comprise hydraulically isolated ports spaced about 10 cm apart below the water table in 3.2-cm inside diameter polyvinyl chloride pipe. Samples will be collected periodically from the sampling points, particularly following recharge events. The timing will be based on results of *in-situ* measurement of water movement through the unsaturated zone. Immunoassay tests will be used as a screening method for detecting the triazine herbicides in ground water. Selected samples identified by immunoassay tests will be analyzed chromatographically to determine changes in the concentrations of atrazine and its metabolites over time.

A hydrologic data base will be designed and managed to relate information of common interest to all scientists working at the Princeton site. It will be essential for the the data manager to coordinate with collaborating researchers from the USGS, USDA, and USEPA who are interested in the common data to determine data needs (input, output, data transfer, processing and analysis, and data access). The data collected at the Princeton site, which are needed in common by other investigators, will be entered, verified, and referenced (1) geographically in three-dimensional space, (2) by source of data, and (3) by time. A geographic information system will be used to prepare base maps and data overlays at various scales.

INTERDISCIPLINARY RESEARCH PLAN

The overall approach to research at the Northern Corn Belt Sand-Plain MSEA is to identify and evaluate key processes and factors affecting the fate of agricultural chemicals in the environment. Multidisciplinary, multiscale research is needed for the various transport, transformation, and phase-transfer processes affecting the fate of agricultural chemicals in the various environmental compartments (atmosphere, soil/root zone, unsaturated zone, saturated zone, and surface water). Researchers from many agencies and areas of expertise will be involved to accomplish this objective.

USDA and university researchers in Minnesota, Wisconsin, North Dakota, and South Dakota will be conducting component research at the Princeton site and all of the satellite sites. Their research focuses on the processes affecting the fate of agricultural chemicals in and above the soil root zone and, to a much lesser extent, the underlying



PRINCETON, MN
5 KILOMETERS
WETLAND
BATTLE
BROOK
ROAD
WOODED AREA
BOUNDARY OF RESEARCH SITE
FARMING SYSTEMS RESEARCH PLOTS
EXPLANATION
USGS RECHARGE RESEARCH SITE
DIRECTION OF GROUND-WATER FLOW
LINEAR-MOVE IRRIGATION SYSTEM
• MULTIPORT SAMPLER
○ WELL
⌀ WELL SAMPLED, 10/90
● IRRIGATION WELL
0
2000 Feet
0
500 Meters

Base from U.S. Geological Survey
Princeton 1:24,000 quadrangle, 1982

The research site is located in the northeast quarter of section 18, townwhip T35N, range R26W.

Figure 2. Proposed plot layout at the Princeton research site.

unsaturated zone. The subjects of their proposed research activities are:

1. Volatilization of agricultural chemicals,
2. Pesticide and nitrogen transformation, transport, and fate,
3. Mass flux and transformation of agricultural chemicals through the unsaturated zone,
4. Relation of preferential flow to the fate and transport of agricultural chemicals,
5. Use of ground-penetrating radar to characterize preferential ground-water flow paths,
6. Biochemistry of carbon and nitrogen mineralization from crop residues,
7. Characterization of crop residue degradation products and their sorption of herbicides,
8. Contribution of soil fauna to the hydraulic characteristics of the unsaturated zone,
9. Impact of surface microrelief on water and associated agricultural chemical infiltration,
10. Effect of mineralogical differences within glacial outwash on the movement of agricultural chemicals,
11. Use of time domain reflectometry to measure soil-water movement in the unsaturated zone,
12. Development of decision-aids software for herbicide use,
13. Development of efficient herbicide use and management practices, and
14. Economic and policy implications of changing farming systems.

Several researchers from the USEPA also plan to conduct research at the Princeton site. The USEPA research is process oriented, focusing on surface-water bodies and the unsaturated and saturated zones. The proposed subjects of USEPA research are:

1. Effect of nonpoint source discharge of agricultural chemicals on surface-water quality,
2. Wetland restoration,
3. Biodegradation of agricultural chemicals in the saturated and unsaturated zones, and
4. Field validation and testing of models simulating the fate and transport of agricultural chemicals.

Researchers from the Geologic and Water Resources Divisions of the USGS plan to conduct process research at the Princeton site. Their focus will be on the unsaturated and saturated zones. The proposed subjects of USGS research activities are:

1. Application of three-dimensional geographic information systems to display changes of agricultural-chemical concentrations in time,
2. Atmospheric transport and deposition of herbicides,
3. The influence of focused recharge on the migration of agricultural chemicals to ground water,
4. The influence of macropores on the flow and transport of agricultural chemicals,
5. Determination of unsaturated-zone properties using vapor-phase techniques,
6. Effects of evapotranspiration on pesticide distributions and transport in the unsaturated zones of northern corn belt sand plains,
7. Tracking of wetting fronts through the unsaturated zone using ground-penetrating radar,
8. Development of geotechnical methods to measure permeability of the unsaturated zone and to determine infiltration potential,
9. Use of gas-flow measurements to investigate macropores in the unsaturated zone,
10. Field testing of an automated solid-phase extraction sampler,
11. Conjugates of herbicides; interactions of natural organic matter with agricultural chemicals,
12. Degradation of atrazine, in depth and time, through the unsaturated and saturated zones, and
13. Effect of agricultural inputs of nitrogen on the nitrogen cycle in a sand-plain watershed in eastern Minnesota.

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ESTIMATES OF GAS-PHASE PHOTOLYSIS FOR ATRAZINE, SIMAZINE, ALACHLOR, AND METOLACHLOR FROM EFFECTIVE ABSORPTION CROSS-SECTION MEASUREMENTS

By William T. Foreman[1], Paul M. Gates[1], Wallace G. DeGiacomo[1], and Larry G. Anderson[2]

ABSTRACT

Ultraviolet-visible absorption cross-sections, in conjunction with solar actinic-flux measurements, may be used to estimate effective photolysis half-lives of organic compounds in the troposphere. A scanning ultraviolet-visible spectrophotometer was used to measure the absorption cross-sections for wavelengths from 285 to 825 nanometers, the region pertinent to solar photolysis of organic contaminants in the troposphere, for atrazine, simazine, alachlor, and metolachlor. The alpha-chloroacetamides, alachlor and metolachlor, were shown to have no absorbance in the wavelength region of solar actinic flux and, consequently, are expected to have extremely long photolysis half-lives in the troposphere. Small absorbances were observed in the range from 285 to 335 nanometers for atrazine and from 285 to 345 nanometers for simazine, indicating photolysis may occur for these two triazine herbicides in the troposphere. However, atmospheric reactions of all four herbicides with photochemical oxidants, like ozone and hydroxyl and nitrate radicals, may prove more important than photolysis as contaminant removal processes.

INTRODUCTION

Volatilization from agricultural fields represents an important source of herbicides in the troposphere, the lowest level of the atmosphere (Comes and Timmons, 1965; Beestman and Deming, 1974; Glotfelty and others, 1989). Kearney and others (1964) reported the volatilization of atrazine and simazine from five different soil types at different soil temperatures. Following application to these soils, 20 to 40 percent of the applied atrazine and < 1 to 10 percent of the applied simazine volatilized in 72 hours at 35 °C (degrees Celsius). The lower volatilization rates reported for simazine compared to atrazine are consistent with their respective vapor pressures, 8.1×10^{-7} Pa (Pascals) and 4.0×10^{-5} Pa at 20 °C (Friedrich and Stammbach, 1964). Alachlor was observed to volatilize from fallow agricultural fields from 1.6 to 115 times faster than atrazine (Glotfelty and others, 1989). Alachlor and metolachlor have vapor pressures, 2.9×10^{-3} Pa at 25 °C and 1.7×10^{-3} Pa at 20 °C, respectively (Herbicide Handbook of the Weed Society of America, 1989), which are approximately two to three orders of magnitude greater than those for atrazine and simazine, and more rapid volatilization from soil is expected for these two chloroacetamide herbicides.

Ambient air measurements indicate that most airborne atrazine and simazine exist in the vapor phase, although the percentage of particle-bound herbicide could rise above 30 percent during colder winter months (Glotfelty and others, 1990). However, alachlor and metolachlor exist almost entirely in the vapor phase (Glotfelty and others, 1990). Wind erosion of soil from herbicide-treated fields appears to play a small role in the introduction of atrazine and simazine into the troposphere, but may be an insignificant mechanism for the more volatile alachor and metolachlor (Glotfelty and others, 1989).

Airborne transport is governed largely by the magnitude of various contaminant removal processes. Physical depositional processes, such as deposition directly from the gas phase (dry gas exchange) to surfaces (such as lakes), dry particle deposition, and wet deposition of gases and particles, influence a contaminant's atmospheric lifetime and can reintroduce the contaminant to surface ecosystems (Bidleman, 1988).

Glotfelty and others (1990) observed fluctuations in concentrations of atrazine, simazine, alachlor, and metolachlor in the air and rain in the Chesapeake Bay region during 1981-82 that correlated with field herbicide-application cycles. Atrazine and simazine were detected year-round in both air and rain samples and appeared sufficiently stable to be transported through the troposphere on at least a regional scale (1,000 kilometers). Wu (1981) also detected atrazine year-round in bulk rain samples collected in the Chesapeake Bay region during 1977-78 and suggested that atrazine might remain in the atmosphere for relatively long periods, thereby enabling it to be carried long distances from the source. Conversely, Glotfelty and others (1990) detected alachlor and metolachlor in air and rain only from April, the beginning of herbicide application, through mid-August, and regional transport for these two herbicides was not indicated. Glotfelty and others (1990) concluded that the very transient nature of alachlor and metolachlor, persisting for only 1 to 2 days in the atmosphere, suggests susceptibility to fairly rapid gas-phase atmospheric degradation processes.

For many contaminants, atmospheric chemical removal processes may be as important, or more so, than physical removal processes. Common chemical removal processes include (1) direct photolysis of a contaminant, in which a contaminant undergoes a reactive process by absorption of solar radiation alone; and (2) photo-initiated oxidant chemistry, in which other photochemical processes generate reactive molecular and free-radical species (the oxidants) that can subsequently react with the contaminant. For organic compounds with low vapor pressures, including the s-triazine and chloroacetamide herbicides, these processes may occur either entirely in the gas phase or with the contaminant sorbed to particles in the atmosphere. Both chemical removal processes rely directly or indirectly on the absorption of

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solar radiation by the contaminant itself (direct photolysis) or by key initiators (which generate the oxidants). The wavelength region of solar actinic flux — the irradiance of sunlight capable of initiating a photochemical reaction pertinent to tropospheric photochemical processes — ranges from ~285 to 800 nm (nanometers). More energetic wavelengths below ~285 nm are absorbed in the upper atmosphere and are not available for photochemical reactions in the troposphere. Solar radiation above 800 nm generally lacks sufficient energy to be involved in most tropospheric photochemical processes (Finlayson-Pitts and Pitts, 1986).

Ideally, direct gas-phase photolysis experiments are conducted by subjecting the contaminant (in the vapor phase), enclosed in a reactor cell, to either natural or articificial sunlight of wavelengths >285 nm. Unfortunately, for low-vapor-pressure compounds, including the four herbicides in this study, direct vapor-phase photolysis measurements are complicated by the inability to generate sufficiently high vapor-phase concentrations to detect the analyte. A previous attempt (Mansour and others, 1981) to determine the direct vapor-phase photolysis of atrazine was unsuccessful because of the inability to detect the low concentration of atrazine in the small-volume photoreactor cell. The use of large exposure chambers and (or) ultrasensitive detection techniques are required to conduct these experiments (Finlayson-Pitts and Pitts, 1986).

Large-chamber experiments, which may provide sufficient mass for analysis, are nontrivial. Therefore, measurement of a contaminant's ultraviolet-visible (UV-vis) spectrum is commonly used to estimate its potential susceptibility to direct photolysis and resultant photolysis half-life (Pitts and others, 1981; Finlayson-Pitts and Pitts, 1986) (see DISCUSSION). However, the same factor that limits gas-phase photolysis experiments also limits the ability to conduct gas-phase absorbance spectra measurements on low-vapor-pressure compounds. As an alternative, spectra of the compound in solution are usually determined. For example, using a 10-mm (millimeter) cell path, an atrazine concentration of 100 ng/μL (nanograms per microliter) in chloroform was shown to have minimal absorption above 290 nm (Gore and others, 1971). These authors also showed that simazine absorbed slightly in the region from 285 to 340 nm. However, the simazine was measured in a 13-mm diameter potassium bromide disc instead of a solvent, and the absorbance spectrum in this solid disc may be shifted to higher wavelengths compared to that observed in the gas phase (see below). Solvents may also affect wavelength maxima and absorbance intensities; consequently, photolysis estimates from nongas-phase spectra are termed "effective" (Finlayson-Pitts and Pitts, 1986).

Understandably, there appear to be no measurements of the direct photolysis of atrazine, simazine, alachlor, or metolachlor sorbed to atmospheric particles. Regardless of whether the atmospheric particles were under suspended (fluidized bed-type) conditions or deposited on a support (such as an air filter), these measurements would represent a substantial experimental challenge. There have been several photolysis investigations of atrazine and simazine sorbed to solid supports that may roughly simulate the surface of atmospheric particles (especially windblown dust or soil). Data from Jordan and others (1964) indicate that half-lives of atrazine and simazine, sorbed onto photometrically uniform filter paper and exposed to sunlight, are on the order of 3 days. Exposure of atrazine, sorbed on silica gel, to artificial sunlight of wavelengths >290 nm reportedly caused a 25-percent loss of herbicide in 48 hours, but only another 10-percent loss occurred after 100 more hours of irradiation (Kempny and others, 1981). These authors also noted that the absorbance spectrum of organic compounds sorbed to silica gel can shift to longer wavelengths, activating the compounds to photolysis. Whether absorbance spectra of the four herbicides shift to longer wavelengths when absorbed to atmospheric particles is unknown.

Several studies have addressed photolysis of atrazine and simazine in both water and water containing solvent sensitizers. For example, Burkhard and Guth (1976) observed a photolysis half-life of ~25 hours for atrazine in water, but this fell to ~5 hours in water containing 1 percent acetone as a sensitizer. Durand and Barcelo (1990) found that only 3 percent of the atrazine and 36 percent of the simazine remained following 3 hours of photolysis in water containing 3 to 4 percent methanol. Implications of these studies to the photolysis lifetimes of atrazine and simazine present on moist atmospheric particles or within cloud droplets are unclear, but the nonsensitized half-life of atrazine and the longer half-life for simazine appears sufficiently long enough to allow for year-round detection of these herbicides in rain as observed by Wu (1981) and Glotfelty and others (1990).

For organic compounds, photo-initiated oxidant removal mechanisms typically involve the three primary atmospheric oxidants, ozone and hydroxyl radical in the daytime and nitrate radical at night (Finlayson-Pitts and Pitts, 1986). The relative importance of these oxidants to photochemical-contaminant degradation reactions largely depend on the reaction rate constant(s) and also usually on the concentration of one or both of the reactants. Ozone concentrations typically range from 0.01 to 0.5 parts per million, with highest concentrations usually observed in large urban areas in the summertime (Finlayson-Pitts and Pitts, 1986). Hydroxyl (OH) radical is an extremely important atmospheric oxidant and appears to drive many of the important daytime photochemical processes. OH radicals react so rapidly with so many different compounds that their atmospheric lifetimes are very short and their concentrations are, therefore, very low, ranging from approximately 4 to 350 parts per quadrillion from the few OH radical measurements (Altshuller, 1989). Nitrate radicals react with many organic compounds at rates often intermediate between those of ozone and OH radicals. Reported nitrate-radical concentrations typically range from <0.002 to 0.4 parts per billion (Finlayson-Pitts and Pitts, 1986).

Investigations of gas-phase oxidant removal processes have usually been limited to small molecules, polycyclic aromatic hydrocarbons being a notable exception (Finlayson-Pitts and Pitts, 1986; Atkinson, 1989). Oxidant degradation studies of both the gas and particle-sorbed phases for the chloroacetamide and triazine herbicides are lacking. Atkinson and others (1987) determined rate constants for the gas-phase reaction of 1,3,5-triazine with ozone and OH radicals, and estimated atmospheric half-lives in a clean and a moderately polluted troposphere of 104 and 52 days, respectively, for reaction with OH radical, and >7.6 and >2.5 years, respectively, for reaction with ozone. They found that reaction of 1,3,5-triazine with gaseous nitric acid was much slower than the reaction with OH radical, but faster than with ozone. Although the OH-radical reaction will dominate removal of 1,3,5-triazine compared to the reaction with the other two oxidants, this removal process is still quite slow in relation to the time necessary for even long-range physical transport in the troposphere. How these oxidant reaction half-lives for 1,3,5-triazine relate to lifetimes of the substituted 1,3,5-triazines, atrazine, and simazine is unclear, but Atkinson and others (1987) suggest that substitution of $-NH_2$ and $-N(CH_3)_2$ (and presumably the alkylamino-groups on atrazine and simazine) may markedly enhance reactivity of the triazine ring.

The overall focus of the present study is to determine the atmospheric lifetimes for atrazine, simazine, alachlor, and metolachlor as a function of the important vapor-phase photochemical degradation processes and to relate these photochemical lifetimes to the potential for atmospheric transport and deposition to ecosystems. This paper presents results of solution phase UV-vis absorption measurements and estimates of the potential occurrence of photolysis and resultant atmospheric lifetimes of these herbicides.

METHODS

Atrazine, simazine, alachlor, and metolachlor were obtained from Crescent Chemical Co., Inc.,[3] Hauppauge, N.Y. Pesticide-grade acetonitrile and cyclohexane were obtained from Burdick and Jackson, Muskegon, Mich.

The UV-vis absorbance spectra of the individual herbicides in solution were measured from 825 to 285 nm using a Cary 17 dual beam scanning spectrophotometer (Varian Instrument Group, Walnut Creek, Calif.). The spectrophotometer was calibrated using 4-nitrophenol obtained from Chemical Procurement Laboratories, Inc., College Point, N.Y. The blank-corrected absorption for p-nitrophenol in acetonitrile measured at concentrations of 2.5, 5.0, 7.5, and 10 ng/µL in a 1-cm (centimeter) path-length quartz cell (Beckman Instruments Inc., Fullerton, Calif.) gave a molar absorptivity of 10,046 (L/mol)/cm (liters per mole per centimeter) at an average maximum wavelength of 307 nm with a standard deviation of 1 nm at half-height and half-width. This molar absorptivity and wavelength maximum are in good agreement with literature values of 10,000 (L/mol)/cm and 311 nm reported by Grasselle (1973) and 11,000 (L/mol)/cm and 318 nm reported by Silverstein and others (1981).

UV-vis absorbance spectra of the herbicides dissolved in solvent were measured in a 10-cm path-length quartz cell (Allen Scientific Glassblowing, Inc., Boulder, Colo.). Alachlor and metolachlor spectra were measured at concentrations of 0.1, 2.5, 5.0, 7.5, and 10 ng/µL, using both acetonitrile and cyclohexane to assess possible solvent effects. Atrazine and simazine spectra were measured at 10, 25, 75 and 100 ng/µL in chloroform and at 10 ng/µL in acetonitrile. Absorbances were scanned at 0.1 or 1.0 absorbance range. Multiple solvent blank spectra were obtained intermittently along with sets of herbicide-spectral measurements to allow for solvent-blank absorbance corrections.

RESULTS AND DISCUSSION

Absorption spectra of these low-vapor-pressure herbicides were measured in solvent for reasons discussed above. Alachlor and metolachlor exhibited no absorbance from 285 to 825 nm in either solvent, strongly suggesting that direct photolysis in the troposphere is not an important removal process for these two herbicides. The reported lack of persistence in the troposphere (Glotfelty and others, 1990), coupled with the apparent lack of photolysis potential, indicates that chemical transformation by the principal tropospheric oxidants, ozone, OH radicals, and (or) nitrate radicals, or possibly by hydrolysis, is a more likely removal mechanism.

Atrazine exhibited a small amount of absorbance in the region from 285 to 335 nm, and simazine exhibited slightly greater absorbance from 285 to 345 nm. Similarities in the absorbance spectra obtained in either chloroform or acetonitrile indicated no solvent effects were occurring. Although the solvent-blank corrected absorbance readings were minimal for atrazine and simazine, the potential for photolysis was indicated. Using this spectral information, the direct photolysis rate constant (k_p) for the reaction

$$\text{compound} + h\nu \rightarrow \text{products}$$

can be estimated from the following relation

$$k_p = \int_{\lambda=285}^{\lambda_i} \sigma_{\lambda} \Phi_{\lambda} J_{\lambda} \, d\lambda \qquad (1)$$

where σ_λ is the absorption cross-section in square centimeters per molecule at wavelength λ, ϕ_λ is the photolysis quantum yield (the fraction of contaminant molecules absorbing light that leads to product formation which is always ≤ 1.0 for atmospheric conditions), J_λ is the solar actinic flux in photons per square centimeter per day at λ, and λ_i is the highest wavelength where light absorption occurs and products are formed.

J_λ is often tabulated as a daily average flux over 10 nm intervals (Pitts and others, 1981) for different times of the year and different latitudes (or zenith angles). Solution of equation 1 is typically approximated by a summation equation

$$k_{p\,max} = \sum_{\lambda=285}^{\lambda_i} \sigma_{\Delta\lambda} J_{\Delta\lambda} \qquad (2)$$

where $\sigma_{\Delta\lambda}$ represents the absorption cross-section averaged over 10-nm intervals, and a maximum quantum yield of unity has been assumed over the region of absorption. $\sigma_{\Delta\lambda}$ values are estimated by computing an average absorbance over each 10-nm wavelength interval ($A_{\Delta\lambda}$) and determining $\sigma_{\Delta\lambda}$ (also called the molar absorptivity) using the Beer-Lambert law

$$A_{\Delta\lambda} = \sigma_{\Delta\lambda} bc \qquad (3)$$

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[3] The use of trade or product names in this paper is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

where, b is the cell path length in centimeter, and c is the analyte concentration in molecules per cubic centimeter. Because path length is fixed, the absorption cross-section is generally calculated from the slope of a linear regression analysis of $A_{\Delta\lambda}$ as a function of concentration.

The resultant $\sigma_{\Delta\lambda}$ and tabulated $J_{\Delta\lambda}$ values are then summed using equation 2 to give $k_{p\,max}$ in inverse days. The contaminant's estimated minimum half-life ($t_{1/2\,min}$) based on this photolysis reaction is then calculated from

$$t_{1/2\,min} = 0.693/k_{p\,max} \qquad (4)$$

This half-life is a minimum estimate because the assumed photolysis quantum yield of unity represents the theoretical maximum. Additional details regarding detemination of absorption cross-sections and estimation of photolysis rate constants are provided in Pitts and others (1981) and Finlayson-Pitts and Pitts (1986).

For atrazine and simazine, average $A_{\Delta\lambda}$ values were computed at 10-nm intervals over the range of observed absorbance beginning at 285 nm for the 10, 25, 75, and 100-ng/μL solutions in chloroform. These average $A_{\Delta\lambda}$ were corrected by subtracting the average $A_{\Delta\lambda}$ observed in the solvent-blank over the corresponding wavelength interval. Blank corrected average $A_{\Delta\lambda}$ were plotted at each concentration (eq. 3) to obtain the $\sigma_{\Delta\lambda}$ at each wavelength interval. Equation 2 was then used to calculate the $k_{p\,max}$ values expected under summer, winter, and equinox periods of solar actinic flux at 30° north latitude. Finally, $t_{1/2\,min}$ was determined using equation 4.

The resultant estimates of the minimum photolysis half-lives were approximately 0.8 (summer solstice), 2.3 (winter solstice), and 1.2 (equinox) days for atrazine and 0.4 (summer solstice), 0.9 (winter solstice), and 0.5 (equinox) days for simazine. These half-lives appear very short, especially when they are considered relative to the potential for even regional-scale physical transport. However, these half-lives represent minimum values because the true photolytic quantum yield over the range of contaminant absorption is unknown. For many organic compounds, ϕ_λ can be substantially less than unity by 1 to 2 orders of magnitude or more (Finlayson-Pitts and Pitts, 1986). If this is the case for these herbicides, the atmospheric half-lives may be orders of magnitude longer than estimated here. Actual photolysis chamber experiments are required to improve estimates of the true ϕ_λ and k_p for these herbicides.

FUTURE STUDIES

The small amount of absorption by atrazine and simazine observed in the low-wavelength region of solar actinic flux suggests a potential for direct photolysis, and initial chamber-photolysis experiments are planned to define the importance of this removal mechanism further. The lack of absorption by alachlor and metolachor suggests that removal by mechanisms other than direct photolysis, such as reaction with photochemical oxidants, hydrolysis, and (or) physical removal, are probably more important for these two herbicides. Chamber studies are planned to measure the transformation rates for the reaction of alachlor with ozone and hydroxyl and nitrate radicals. Alachlor will be tested first because of its higher vapor pressure compared to the two triazine herbicides. The experimentally determined reaction rates will be used to estimate the relative importance of alachlor oxidation reactions compared to other physical removal processes. Results from these initial triazine-photolysis and alachlor-oxidant experiments will provide further direction in this exploration of herbicide atmospheric photochemistry.

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LITERATURE REVIEW OF VAPOR PRESSURE DATA FOR SOME CHLORINATED TRIAZINE AND ACETAMIDE HERBICIDES

By William T. Foreman[1] and Wallace G. DeGiacomo[1]

ABSTRACT

A comprehensive review of the literature has been undertaken to ascertain the original experimentally determined vapor pressure data for atrazine and four of its degradation products, desethylatrazine, desisopropylatrazine, desethyldesisopropylatrazine, and hydroxyatrazine, along with four additional herbicides, simazine, metribuzin, alachlor, and metolachlor. Many of the reported vapor pressure values can be traced back to only one or two original experimental determinations. In other cases, the values given are incompletely cited. To date, only two citations containing original experimental data have been found for atrazine and one citation found for simazine. There appears to be no specific vapor pressure data available for any of the four major degradation products of atrazine. Vapor pressure data reported in the literature for alachlor, metolachlor, and metribuzin appear to originate from manufacturer's data, the original experimental reports from which have not yet been ascertained.

INTRODUCTION

Knowledge of accurate saturation vapor pressures and solubilities of organic contaminants at ambient conditions is critical to understanding and modeling their environmental transport and fate. These physical properties are extensively used in determinations or estimations of other partition coefficients, including vapor-particle and sediment-water partition coefficients. From vapor pressure and solubility data, one can also calculate the Henry's Law constant, the value of which is useful for estimating, for example, an organic pollutant's (1) movement across the air-water interface, (2) vapor-phase dissolution into rain, and (3) volatilization from moist soil. Solubility and vapor pressure data also are useful in the design and implementation of proper sampling and analytical methods.

A project has been undertaken to determine some important physical properties, including vapor pressure, melting point, water solubility, and estimated Henry's Law constant for the herbicides atrazine (and four of its degradation products), simazine, metribuzin, alachlor, and metolachlor, all of which are widely used in the mid-continent of the United States. In order to determine what physical property information is unavailable and thus needed, a comprehensive review of the published literature has been undertaken to obtain and evaluate original experimental data. This paper presents results of the literature search to date for original experimental vapor pressure data, and discusses several potential pitfalls researchers may encounter in locating physical property data and in using these data in research.

DISCUSSION

When seeking physical property data such as vapor pressures for use in research, scientists commonly turn to reference handbooks, textbooks, review articles, and material safety data sheets that summarize these findings. Unfortunately, the data may be presented (1) with a citation of a source different from that of the original experimental work, (2) with a citation indicating that "the manufacturer" is the source with no company name given, (3) in a manner that does not make it clear whether a source is cited for the specific property or value, or (4) with no apparent citation at all. Several other factors can complicate the search for a compound's vapor pressure, such as variations in the units of vapor pressure and in the number of significant figures quoted. Also, vapor pressure is highly dependent on temperature and, therefore, the temperature must be reported along with the vapor pressure value. As a consequence, a casual survey of the literature might lead a researcher to believe that there are a large number of original determinations of a compound's vapor pressure, all showing similar agreement and, thereby, misleadingly providing an artificially enhanced degree of confidence in the accuracy of the values. However, there may, in fact, be only one or two sets of original experimental determinations.

As an illustration of the potential problems one may encounter in searching for physical property data, table 1 presents vapor pressure data reported in a variety of literature sources for atrazine and simazine. To date, only two references of original experimentally determined vapor pressures for atrazine have been located. The original data of Friedrich and Stammbach (1964) is from the manufacturer of atrazine, because these authors were affiliated with the laboratories of J.R. Geigy[2] (now Ciba-Geigy, AG). These authors reported an extrapolated (see below) vapor pressure of 3.0×10^{-7} mm Hg (millimeters of mercury) (or, in pressure units of pascals, 4.0×10^{-5} Pa) at 20 °C (degrees Celsius). The other original experimental data for atrazine is from Grayson and Fosbraey (1982) and, except for their data, all the remaining data in table 1 likely have originated from the data of Friedrich and Stammbach (1964).

Note the differences in units of vapor pressure, number of significant figures, and the temperature for the various values reported (table 1). Without careful examination, these kinds of differences can lead to both confusion and misinterpretation regarding the total number of true original experimental values. This confusion is further confounded by improper or incomplete citation to the original data source. In some cases, source citation is missing or unclear. In other cases, the reported source is not the original research. For example, Glotfelty and others (1990) cite the extensive compilation of pesticide physical property data by Suntio and others (1988) who, in turn, cite Spencer (1976) as the source for the vapor pressure of atrazine. However, Spencer (1976) cites the original work of Friedrich and Stammbach (1964). Luckily in this case, the citations ultimately lead back (if pursued) to the original experimental research. In other cases, the citations dead end. Considering simazine for example (table 1), Suntio and others (1988) cite Kahn (1980) as the vapor pressure source. However, Kahn (1980) does not contain the original experimental research nor does it provide a clear citation to the original source. To date, this literature search has revealed only the Friedrich and Stammbach (1964) paper as an original source of vapor pressure data for simazine.

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[2] The use of firm names in this paper is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

The original experimentally determined vapor pressure data for atrazine and simazine are summarized in table 2. Grayson and Fosbraey (1982) and Friedrich and Stammbach (1964) used the gas saturation method for determining the vapor pressures of these compounds. Gas saturation is usually the method of choice for low vapor pressure compounds and its use has been approved by the U.S. Environmental Protection Agency (Federal Register, 1980). Gas saturation measurements are made at a constant temperature by passing a slow steam of air or nitrogen through a column of glass beads or sand that has been coated with the compound of interest. The compound-saturated gas stream is then passed through a collection device (typically a solid sorbent trap) that quantitatively removes the compound from the gas stream.

Table 1. *Examples of vapor pressure values used in the literature for atrazine and simazine*

[Pa, pascals; mm Hg, millimeters of mercury; °C, degrees Celsius; mPa, millipascals; mbar, millibar; nPa, nanopascals]

Atrazine

Reference where value cited	Reported vapor pressure, units given (at temperature)		Corresponding vapor pressure, (Pa)	Reported source
Friedrich and Stammbach, 1964	3.0×10^{-7} mm Hg	(20 °C)	4.0×10^{-5}	Original data[1]
Gunther and Gunther, 1970	3×10^{-7} mm Hg	(20 °C)	4×10^{-5}	J.R. Geigy[1]
Spencer, 1976	3.0×10^{-7} mm Hg	(20 °C)	4.0×10^{-5}	Friedrich and Stammbach, 1964
Worthing, 1979	3×10^{-7} mm Hg	(20 °C)	4×10^{-5}	Unclear[2]
Worthing, 1987	4×10^{-2} mPa	(20 °C)	4×10^{-5}	Unclear[2]
Weber and others, 1980	0.3×10^{-6} mm Hg	(20 °C)	4×10^{-5}	None
Kahn, 1980	3.0×10^{-7} mm Hg	(20 °C)	4.0×10^{-5}	None
Grayson and Fosbraey, 1982	3.7×10^{-5} Pa	(20 °C)	3.7×10^{-5}	Original data
The Agrochemicals Handbook, 1983	4×10^{-7} mbar	(20 °C)	4×10^{-5}	None
The Agrochemicals Handbook, 1987	4×10^{-2} mPa	(20 °C)	4×10^{-5}	None
Baker and Johnson, 1984	6.5×10^{-7} mm Hg	(25 °C)	8.7×10^{-5} (25 °C)	Herbicide Handbook, 1974
Dobbs, 1984	4.0×10^{-5} Pa	(20 °C)	4.0×10^{-5}	Worthing, 1979
MSDS, 1987[3]	4×10^{-7} mbar	(20 °C)	4×10^{-5}	None
MSDS, 1987[4]	3.0×10^{-7} mm Hg	(20 °C)	4.0×10^{-5}	None[1]
MSDS, 1989[5]	3×10^{-7} mm Hg	(20 °C)	4×10^{-5}	None
Suntio and others, 1988	3.99×10^{-5} Pa	(20 °C)	3.99×10^{-5}	Spencer, 1976
Herbicide Handbook, 1989	3.0×10^{-7} mm Hg	(20 °C)	4.0×10^{-5}	Ciba-Geigy[1]
Glotfelty and others, 1989	6.6×10^{-7} mm Hg	(NR[6])	8.8×10^{-5} (25 °C)	Friedrich and Stammbach, 1964
Glotfelty and others, 1990	4×10^{-2} mPa	(20 °C)	4×10^{-5}	Suntio and others, 1988

Simazine

Reference where value cited	Reported vapor pressure, units given (at temperature)		Corresponding vapor pressure, (Pa)	Reported source
Friedrich and Stammbach, 1964	6.1×10^{-9} mm Hg	(20°C)	8.1×10^{-7}	Original data[1]
Gunther and Gunther, 1970	6.1×10^{-9} mm Hg	(20 °C)	8.1×10^{-7}	J.R. Geigy[1]
Worthing, 1979	6.1×10^{-9} mm Hg	(20°C)	8.1×10^{-7}	Unclear[2]
Worthing, 1987	8.1×10^{-7} Pa	(20°C)	8.1×10^{-7}	Unclear[2]
Weber and others, 1980	6×10^{-9} mm Hg	(20 °C)	8×10^{-7}	None
Kahn, 1980	6.1×10^{-9} mm Hg	(20 °C)	8.1×10^{-7}	None
The Agrochemicals Handbook, 1983	8.1×10^{-9} mbar	(20 °C)	8.1×10^{-7}	None
The Agrochemicals Handbook, 1987	$8.1 \times 10^{+2}$ nPa	(20 °C)	8.1×10^{-7}	None
MSDS, 1987[3]	6.1×10^{-9} mm Hg	(20 °C)	8.1×10^{-7}	None
MSDS, 1988[5]	8.1×10^{-9} mbar	(20 °C)	8.1×10^{-7}	None
Suntio and others, 1988	8.13×10^{-7} Pa	(20 °C)	8.13×10^{-7}	Kahn,1980
Herbicide Handbook, 1989	6.1×10^{-9} mm Hg	(20°C)	8.1×10^{-7}	Ciba-Geigy[1]
Glotfelty and others, 1989	1.5×10^{-8} mm Hg	(NR[6])	2.0×10^{-6} (25 °C)	Friedrich and Stammbach, 1964

[1] Data are manufacturers because Friedrich and Stammbach (1964) are from the laboratories of J.R. Geigy (now Ciba-Giegy AG).
[2] Source unclear, may be manufacturer.
[3] Material Safety Data Sheet from Riedel-de Haen AG, 1987.
[4] Material Safety Data Sheet from Ciba-Geigy Corp.,1987.
[5] Material Safety Data Sheet from Occupational Health Services, Inc., 1988 and 1989.
[6] NR, temperature not reported but apparently is 25 °C based on data of Friedrich and Stammbach, 1964.

The collection device contents are then analyzed instrumentally and the vapor pressure calculated from the ideal gas law.

Gas saturation measurements are usually made over a range of temperatures, often above ambient temperature to speed up the measurement process. For example, Grayson and Fosbraey (1982) measured the vapor pressure of atrazine at seven different temperatures ranging from 51.0 to 81.5 °C (table 2). (Note: These authors also determined vapor pressures for four other pesticides, aldrin, dieldrin, dicrotophos, and cyanazine, which are not reported here.) Friedrich and Stammbach (1964) measured vapor pressures for atrazine and simazine at six different temperatures ranging from 50 to 130 °C. (Note: These authors determined vapor pressures for eight other symmetrical triazines: propazine, atratone, prometone, simetone, ametryne, prometryne, simetryne, and norametryne, which are not reported here.) If the temperature range over which the gas saturation measurements are conducted is fairly close to ambient temperatures, then this higher-temperature vapor pressure data can be extrapolated to lower ambient temperatures using an approximation of the Clausius-Clapeyron equation (Levine, 1978):

$$\frac{d\ln P}{dT} \approx \frac{\Delta H_v}{RT^2} \tag{1}$$

where P is the vapor pressure, ΔH_v is the molar enthalpy of vaporization, R is the gas constant and T is the temperature in Kelvin. Making the assumption that ΔH_v is constant over the temperature range of interest, then integration of equation 1 yields

$$\ln\frac{P_2}{P_1} \approx -\frac{\Delta H_v}{R}\left[\frac{1}{T_2}-\frac{1}{T_1}\right] \tag{2}$$

If P_1 is 1 atmosphere (= 101,325 Pa = 760 mm Hg), then T_1 is the normal boiling point, T_b. Dropping the subscripts gives

$$\ln(P/1\ \text{atmosphere}) \approx -(\Delta H_v/R)(1/T) + \Delta H_v/RT_b = (-A/T)+B \tag{3}$$

where $A = \Delta H_v/R$, and $B = \Delta H_v/RT_b$, a constant. A plot of ln P as a function of 1/T using the experimentally determined data from gas saturation experiments should result in a near linear relation, especially over a fairly small temperature range, the slope of which can be used to calculate the enthalpy of vaporization. Equation 3 is a form of the Clausius-Clapeyron equation commonly used to extrapolate vapor pressure values at different temperatures.

In table 2, the A and B parameters of regression from the experimental data of Grayson and Fosbraey (1982) and Friedrich and Stammbach (1964) are presented. The resulting parameter values obtained depend on the units of pressure and the form of equation 3 used (that is, whether using pascals and natural logarithms as did Grayson and Fosbraey or millimeters of Hg and base 10 logarithms, as did Friedrich and Stammbach). Because of these differences, the reported atrazine regression parameters shown in table 2 are not equivalent, and this is another feature to recognize when evaluating vapor pressure data in the literature. Grayson and Fosbraey provided tabulated vapor pressures in pascals at their experimental conditions, and conversion of their data to millimeters of Hg units and application of the base 10 logarithm form of equation 3 yielded values for A and B (given in parentheses in table 2) remarkably similar to those of Friedrich and Stammbach. In both cases, these researchers extrapolated their gas saturation data at higher temperatures to ambient conditions of 20 °C to provide the values that, at least in the case of Friedrich and Stammbach, are widely reported in the literature (table 1). These equation 3 parameters can also be used to calculate the vapor pressure at other temperatures of environmental interest, as has been done for 0 °C in table 2.

The literature search of vapor pressure data for metribuzin, alachlor and metolachlor has provided the same types of variabilities in reported values as were observed for atrazine and simazine (table 1). The search thus far has led to manufacturers' derived data which are reported by the Herbicide Handbook of the Weed Society of America (1989) as $<1.3 \times 10^{-3}$ Pa at 20 °C for metribuzin, 2.93×10^{-3} Pa at 25 °C for alachlor, and 1.7×10^{-3} Pa at 20 °C for metolachlor. The search continues to obtain and evaluate original vapor pressure data for these three herbicides.

The vapor pressure and solubility data obtained from the material safety data sheets for the four atrazine degradation products, desethylatrazine, desisopropylatrazine, desethyldesisopropylatrazine, and hydroxyatrazine are shown in table 3. Apparently, minimal physical property information is known for the atrazine degradation products, and efforts to determine vapor pressures and solubilities for these compounds are warranted.

Table 2. *Experimentally determined vapor pressure data for atrazine and simazine*

[Pa, pascals; °C, degree Celsius; GS, gas saturation]

Compound	Reference	Method	Temperature[1] range (°C)	Equation parameters A	Equation parameters B	Calculated vapor pressure (Pa)[2] at 20 °C	Calculated vapor pressure (Pa)[2] at 0 °C
Atrazine	Grayson and Fosbraey (1982)	GS	51–81	[3]13,778 [4](6,003)	36.8 (13.9)	3.7×10^{-5}	1.2×10^{-6}
Atrazine	Friedrich and Stammbach (1964)	GS	50–130	[5] 5,945	13.766	4.0×10^{-5}	1.3×10^{-6}
Simazine	Friedrich and Stammbach (1964)	GS	50–130	[5] 6,833	15.107	8.1×10^{-7}	1.6×10^{-8}

[1] Experimental temperature range over which gas saturation vapor pressure measurements were determined.

[2] Vapor pressures calculated using the reported equation parameters shown determined from gas saturation data.

[3] Reported parameters determined using units of pascals for the equation: ln (vapor pressure) = B - A/T.

[4] Regression parameters determined after conversion of the vapor pressure data of Grayson and Fosbraey to mm Hg and using the equation: $\log_{10}$ (vapor pressure) = B - A/T.

[5] Reported parameters determined using millimeters of mercury for the equation: $\log_{10}$ (vapor pressure) = B - A/T.

Table 3. *Reported vapor pressure, solubility, and melting point data for four atrazine degradation products*[1]

Compound	Vapor pressure	Water solubility	Melting point (degrees Celsius)
Desethylatrazine	Not available	Very slightly soluble	132–134 (decomposes)
Desisopropylatrazine	Very low	Insoluble	170–172
Desethyldesisopropylatrazine	Very low	Insoluble	>320
Hydroxyatrazine	Not available	Very slightly soluble	>320

[1] Data from Material Safety Data Sheets for these four compounds from Riedel-de Haen, AG.

FUTURE

The search continues for original vapor pressure, melting point, and solubility data in the literature. In addition, vapor pressure measurements using the gas saturation method have been undertaken on atrazine to evaluate the performance of our experimental procedure by comparing results with previous experimental data (table 2). Vapor pressure measurements will then follow for those compounds for which data are limited, especially metribuzin and the atrazine degradation compounds. These measurements will be made over a range of at least four temperatures (typically from -5 to 35 °C) covering much of the ambient range, to enable calculation of the enthalpy of vaporization and the vapor pressure at other temperatures of interest. If possible, the enthalpy and entropy of fusion for the compounds will be determined by differential scanning calorimetry or by alternative approaches when necessary, because the entropy of fusion data are critical for estimating the subcooled liquid-phase vapor pressures and solubilities for compounds that are solids at ambient conditions. These subcooled liquid-phase properties are the relevant properties to use in most models of contaminant partitioning between environmental compartments (Chiou and others, 1982; Bidleman and Foreman, 1987).

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RELATION OF SELECTED WATER-QUALITY CONSTITUENTS TO RIVER STAGE IN THE CEDAR RIVER, IOWA

By Peter M. Schulmeyer[1]

ABSTRACT

Water samples collected from the Cedar River in east-central Iowa indicate that measured values of specific conductance and pH and concentrations of dissolved oxygen, nitrate, and atrazine are related to changes in river stage. Samples were collected monthly from May 1989 through July 1990; daily samples were collected during periods of storm runoff n March and May 1990. Specific conductance, pH, and concentrations of dissolved oxygen are apparently inversely related to the measured stage of the river, whereas concentrations of atrazine and nitrate are apparently directly related.

The apparent inverse relation of specific conductance to the measured stage of the river may be the result of the dilution of the ground-water component of riverflow with surface-water runoff, which generally has less specific conductance and pH than ground water. The apparent inverse relation of pH and concentrations of dissolved oxygen to the measured stage of the river may be the result of the dilution of dissolved oxygen and carbon dioxide, in the stream, by surface-water runoff.

Nitrate and atrazine concentrations, both of which are agricultural chemicals, correlated with time of application as well as with river stage. However, nitrate concentrations peaked several days after the peak stage of the river. These correlations may be the result of the leaching of these chemicals from agricultural areas during periods of storm runoff. Sample concentrations collected after application of these chemicals were larger than those collected before application.

INTRODUCTION

Streamflow is derived from surface-water and ground-water sources. Variations in the volume of water contributed by these sources over time determine the chemical and physical characteristics of the streamwater quality. During stable, low river stage, much of the streamflow is derived from ground-water sources. The characteristics of streamwater at stable, low stage resemble those of the ground water that is predominant in the stream. Surface water that enters the stream during periods of storm runoff dilutes the streamflow and changes the chemical and physical characteristics of the streamwater. As the stream receives increasing amounts of surface-water runoff, the stage rises, and the characteristics of the streamwater quality begin to resemble those of the surface water entering the stream.

This paper documents the results of a study conducted during 1989 and 1990 to assess the transport and storage of agricultural chemicals in alluvial aquifers as the result of the release of bank storage of riverwater during periods of storm runoff. The presentation of data describes the effects of rising and falling river stage on specific conductance, pH, and concentrations of dissolved oxygen, atrazine, and nitrate in the Cedar River, east-central Iowa.

Location and Description of Study Site

The study site is located in an unfarmed area next to the Cedar River (fig. 1). Bedrock in the basin consists of dolomite, limestone, and small quantities of shale; the bedrock is exposed in the river valley in some areas. The Iowan Erosion Surface is a pre-Illinoian glacial-drift deposit that covers much of the basin. The basin's upper reaches are covered by Wisconsin-age Cary drift (Des Monies lobe). Thickness of the glacial drift ranges from 0 to 120 m (meters).

Upstream from the study site, the Cedar River drains approximately 10,475 square kilometers of mostly agricultural land. Precipitation in the Cedar River basin ranges from 76 to 84 centimeters annually but varies considerably from year to year. Ground-water contribution to the Cedar River is estimated to be between 56 to 80 percent of total discharge during normal years.

Sample Collection and Analysis

Data from the study site is limited to surface-water samples collected from May 1989 through July 1990, to serve as a single-point characterization of the water quality of the Cedar River. Sample collection was done on a regular monthly schedule and daily during periods of storm runoff that occurred before and after the application of farm chemicals. Specific conductance, pH, and dissolved oxygen concentrations were immediately measured at streamside. Nitrate and atrazine samples were collected with a vertically integrating hand sampler in the deepest, swiftest part of the river when it could be waded, and during high stage from an alternate collection site at a bridge approximately 2.8 kilometers upstream from the study site (fig. 1). The samples were collected and divided equally between three 1-liter bottles until filled. The samples then were filtered through a stainless-steel or aluminum filter holder using a 0.45-µm (micrometer) cellulose acetate filter for the nitrate samples and a 1-µm glass microfiber filter for the atrazine samples. The sampler and filter holder were decontaminated before and after use with organic-free distilled water. One nitrate and two atrazine samples were collected during each sampling event. Nitrate samples were preserved using mercuric chloride, and all samples were chilled and sent to laboratories. The nitrate samples were analyzed at the U.S. Geological Survey National Water Quality Laboratory in Denver, Colo., and the herbicide samples were analyzed at the U.S.Geological Survey laboratory in Lawrence, Kans., by gas chromatography-mass spectrometry (Thurman and others, 1990). River stage was recorded at 15-minute intervals by means of a hydrologic fluidgage.

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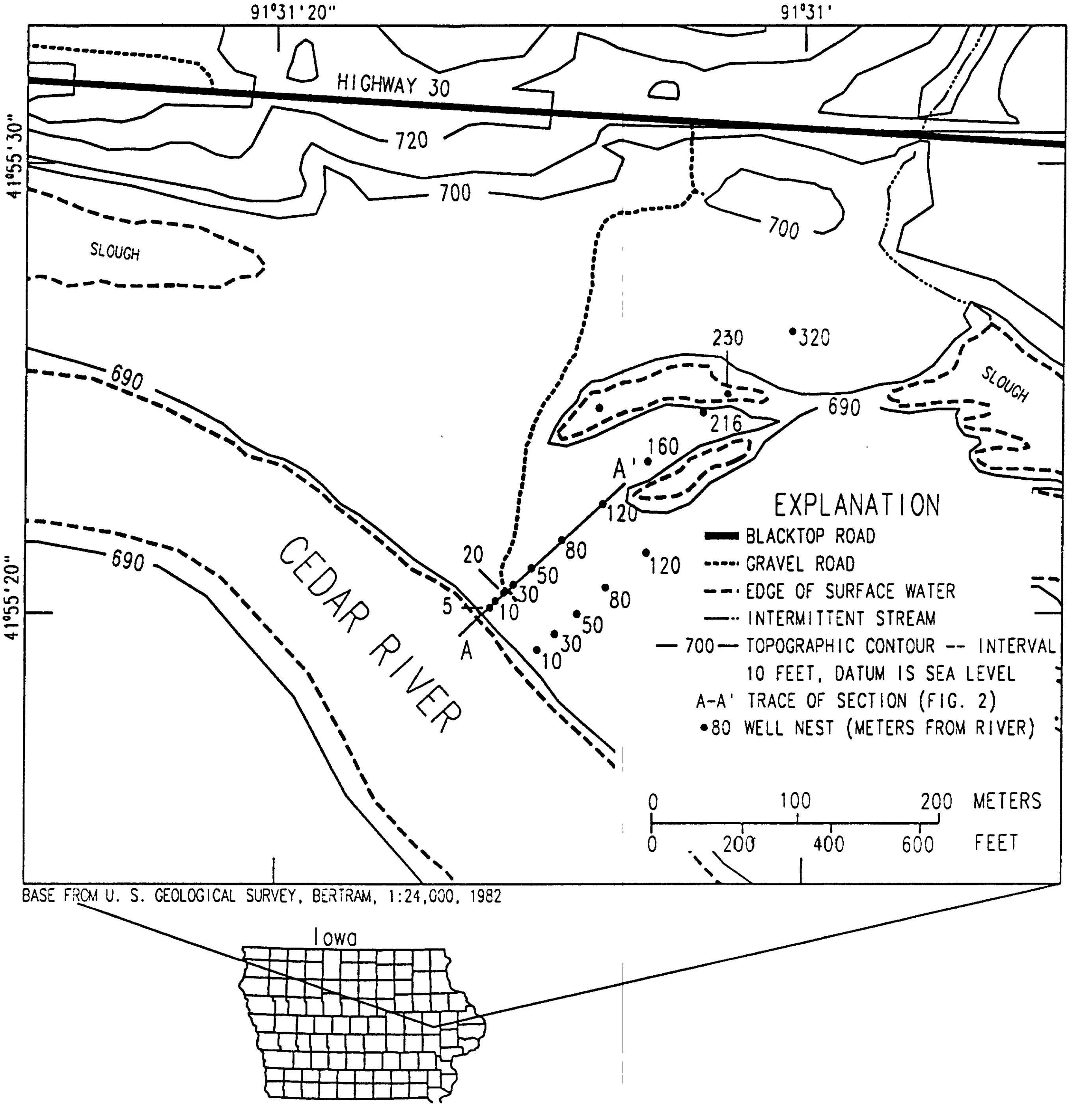
[1] U.S. Geological Survey, Iowa City, Iowa.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216
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EXPLANATION
BLACKTOP ROAD
GRAVEL ROAD
EDGE OF SURFACE WATER
INTERMITTENT STREAM
— 700 — TOPOGRAPHIC CONTOUR -- INTERVAL 10 FEET, DATUM IS SEA LEVEL
A-A' TRACE OF SECTION (FIG. 2)
•80 WELL NEST (METERS FROM RIVER)
0 100 200 METERS
0 200 400 600 FEET
Iowa

BASE FROM U. S. GEOLOGICAL SURVEY, BERTRAM, 1:24,000, 1982

Figure 1. Location of study site in east-central Iowa.

DISCUSSION

Streams carry water that consists of a base-flow fraction and a direct-runoff fraction . The base-flow fraction is made up of ground water that infiltrates into the stream. The direct-runoff fraction enters the stream during or soon after periods of precipitation. The base-flow fraction generally is characterized by a specific conductance larger than that of the direct-runoff fraction. This large specific conductance is associated with increased concentrations of dissolved solids resulting from a comparetively long residence time in the soil and bedrock; thus, as the direct-runoff fraction increases in proportion to the base-flow fraction of the stream, the specific conductance decreases as the stage increases.

This inverse relation of specific conductance to stage during periods of surface runoff is represented in figure 2. The data show that, on March 8, 1990, specific conductance was 833 µS/cm (microsiemens per centimeter at 25 degrees Celsius), and stage was 207.05 m above sea level. Specific conductance was 462 µS/cm on March 17, 1990, and stage was 208.89 m above sea level. On April 3, 1990, specific conductance was 775 µS/cm and stage was 207.49 m above sea level. Similar results occurred for periods of surface runoff in September 1989 and May 1990. These results can be attributed to the dilution of the base-flow fraction of streamwater with increasing volumes of surface runoff that generally has lower specific conductance than ground water.

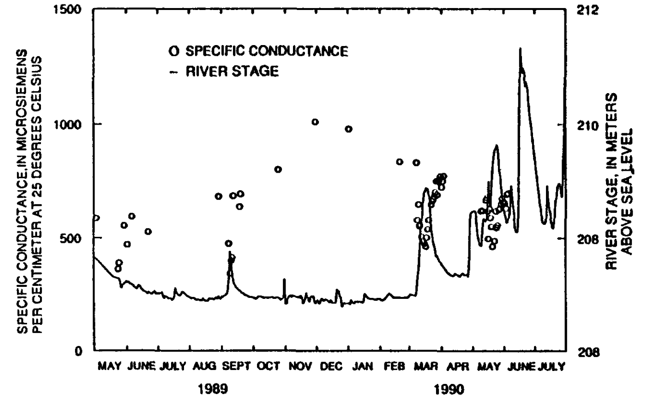

Figure 2. Specific-conductance values and stage of the Cedar River at study site, May 1989 to July 1990.

A similar relation for pH and concentrations of dissolved oxygen is shown in figures 3 and 4. On March 8,1990, the pH was 8.4 and on March 17, 1990, it was 7.7. The concentration of dissolved oxygen was 15.80 mg/L (milligrams per liter) on March 8,1990, and 9.60 mg/L on March 17, 1990. Stage for these dates was 207.05 m to 208.89 m above sea level, respectively. The decrease in pH and concentration of dissolved oxygen during periods of surface runoff can be attributed to the dilution of the dissolved oxygen and carbon dioxide in the stream that results from the microbial process that generally occurs in the river during stable-flow conditions.

Concentrations of nitrate and atrazine related to river stage are shown in figures 5 and 6. As the stage increased during periods of surface runoff, the concentrations of these agricultural chemicals increased. A correlation with time of application also appears in the data between periods of preapplication and postapplication surface runoff (fig. 5). The two chemicals are applied directly to the land surface. Water, generally in the form of precipitation, extracts these chemicals from the soil . The chemicals are mobilized in surface runoff and subsurface flow, which transports them into the streams that drain the basin. The period of preapplication surface runoff occurred during March 8-April 3, 1990, and postapplication surface runoff occurred during May 9-June 4, 1990.

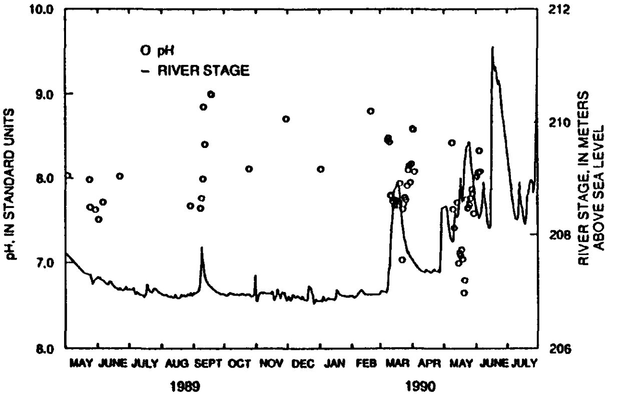

Figure 3. pH values and stage of the Cedar River at study site, May 1989 to July 1990.

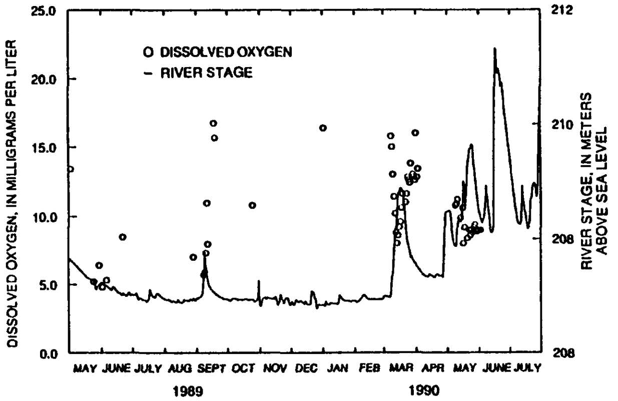

Figure 4. Dissolved-oxygen concentration and stage of the Cedar River at study site, May 1989 to July 1990.

Peak concentrations of nitrate occurred 2 to 7 days after the peak of the river stage. For the period of preapplication surface runoff, the concentration of nitrate plus nitrite as nitrogen was 3.50 mg/L, and river stage was 207.05 m above sea level on March 8, 1990. The river stage peaked on March 17, 1990, at 208.89 m above sea level, whereas nitrate peaked 5 days later at 11.00 mg/L on March 23, 1990. During the period of postapplication surface runoff, the concentration of nitrate plus nitrite as nitrogen was 7.70 mg/L on May 9, 1990, and river stage was 207.87 m above sea level. As streamflow increased, the river peaked three separate times, as can be seen on the rising limb of the hydrograph in figure 6. On May 12, 1990, the river stage was 208.38 m above sea level; on May 17, 1990, the river stage was 209.01 m above sea level; and on May 25,1990, stage reached its maximum for this period at 209.65 m above sea level.

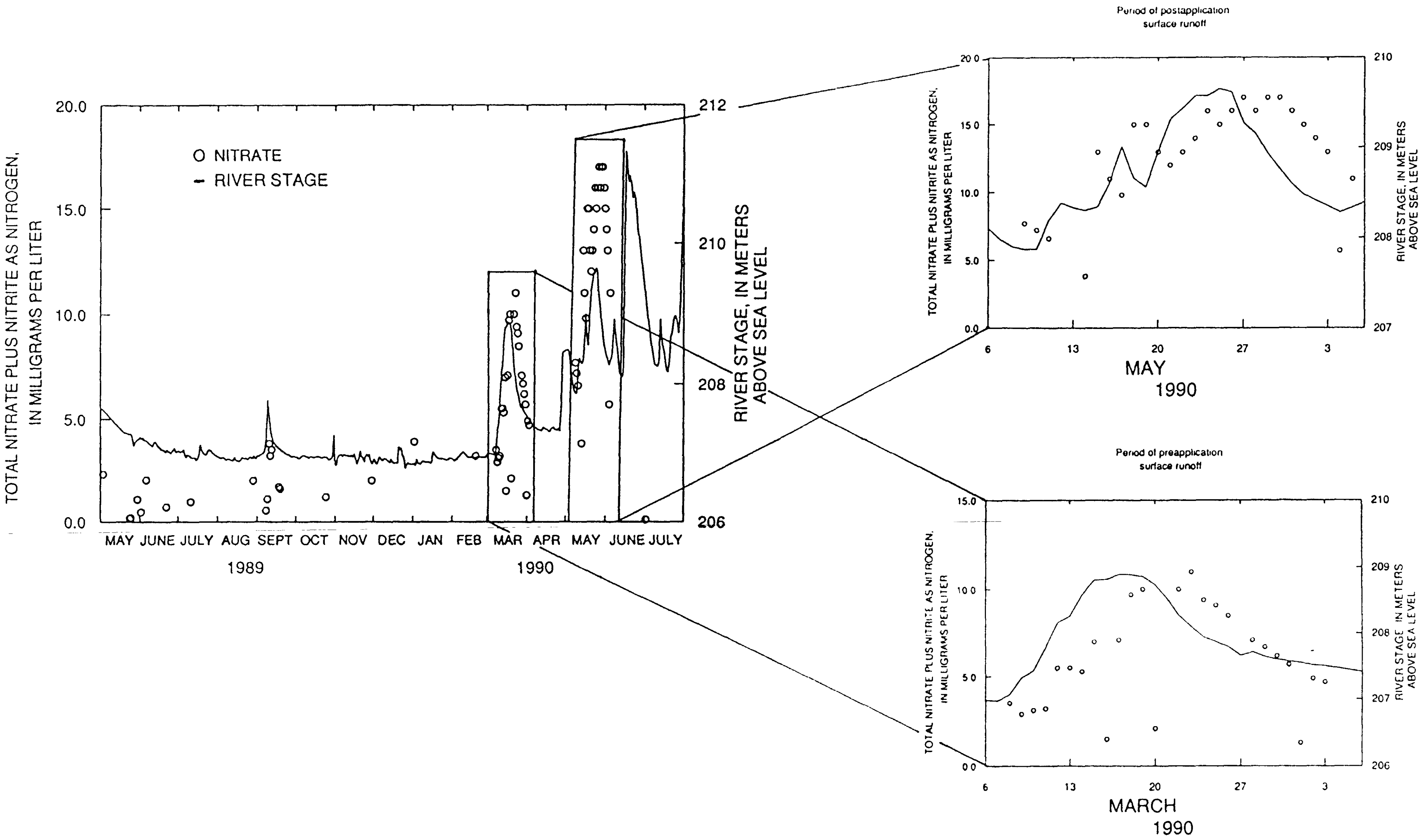

Figure 5. Nitrate concentration and stage of the Cedar River at study site, May 1989 to July 1990.

Nitrate concentrations were 13.00 mg/L on May 15,1990, 15.00 mg/L on May 19, 1990, and 17.00 mg/L on May 30, 1990. This time lag in concentration peaks has been observed by Kissel and others, (1976). The time lag may result from the difference when direct stormwater runoff reaches the stream and when effluent, from field tiles and (or) subsurface flow that has reemerged as ground-water discharge, reaches the stream.

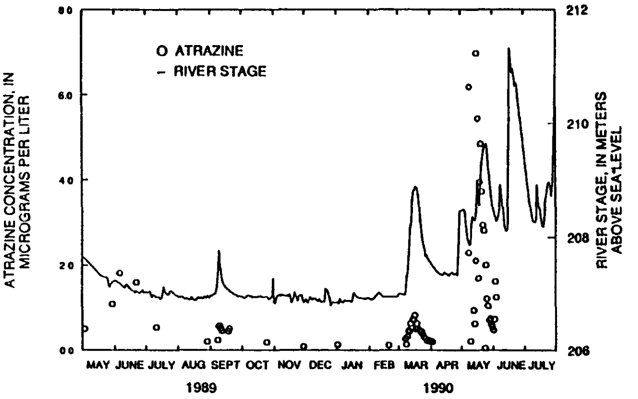

Figure 6. Atrazine concentration and stage of the Cedar River at study site, May 1989 to July 1990.

On March 8, 1990, during the period of preapplication surface runoff, the concentration of atrazine was 0.28 µg/L (micrograms per liter) and was 0.82 µg/L on March 17, 1990. River stage was 207.05 m and 208.89 m above sea level for the same dates. During the period of postapplication surface runoff, atrazine concentration was 2.31µg/L on May 9, 1990, and 6.98 µg/L on May 17, 1990, while stage was 207.87 m and 209.01 m above sea level for the same dates.

SUMMARY

Flow in the Cedar River consists of a ground-water fraction and a surface-water fraction. During stable lowflow the chemical and physical characteristics of the water in the stream resemble those of ground water. The values for specific conductance and pH tend to be large and the concentrations of nitrate and atrazine are smaller. Concentrations of dissolved oxygen also tend to be large during periods of stable lowflow. During periods of storm runoff, the chemical and physical characteristics of the water in the stream resemble those of surface water. When the river stage rises because of storm runoff, specific conductance, pH, and concentrations of dissolved oxygen decrease while concentrations of nitrate and atrazine increase. Dilution of the stream by surface-water runoff is a major factor in the chemical and physical changes of the stream. Specific conductance, pH, and concentrations of dissolved oxygen changed inversely with changes in the river stage due to surface-water runoff. Changes in the concentrations of nitrate and atrazine correlate with increases in river stage as a result of surface-water runoff.

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PHOTOLYTIC DEGRADATION OF ATRAZINE IN THE CEDAR RIVER, IOWA, AND ITS TRIBUTARIES

By Marvin C. Goldberg[1], Kirkwood M. Cunningham[1], *and* Paul J. Squillace[2]

ABSTRACT

One of the anthropogenic materials entering the Cedar River, Iowa, is atrazine. This herbicide is applied as an agricultural additive and, as a consequence of rainfall-runoff, feeds into tributaries of the Cedar River, Iowa, from which it is carried to the main stem of the river. Water samples collected from the tributaries and the main stem were photolyzed in a sunlight simulator to evaluate the effect of sunlight-induced degradation of this material as it is transported to the main stem of the river. The loss of atrazine was measured as a function of photon flux and it was found that the half-lives of degradation, in midday sunlight at 40° latitude, ranged from 38 to 318 hours at the 11 sites tested. A correlation was found between increased concentrations of nitrate and increased rates of photolytic degradation. Nitrate is activated by sunlight to produce hydroxyl radical, thus, the mechanism for photolytic decomposition is most likely an indirect photolysis where the nitrate ion is an a intermediate sensitizer producing hydroxyl radical that then reacts with s-atrazine as follows:

.OH + Atrazine → 2,4-diamino-6-hydroxy-N-ethyl-N'-(1-methylethyl) -1,3,5- triazine) + Cl
after several steps→ Cyanuric Acid.

Photolytic degradation is site specific. Almost all of the photolytic degradation occurs in the tributaries. Very low rates of photolysis were measured in the main stem. Nitrate also is added to the natural environment in the form of fertilizer on a schedule determined by agricultural necessity; thus, the photolytic degradation of atrazine in tributaries to the Cedar River, Iowa, is controlled by agricultural prerogatives.

INTRODUCTION

Sunlight not only supplies energy for photosynthesis and other biochemical reactions but also is the energy source for abiotic chemical processes in environmental systems. (Roof, 1982, p. 43-72). The literature regarding reaction rates, intermediate species, reaction sequences, free radical sequences and oxidation-reduction and degradation reactions has been accumulating at an accelerating rate in the past few years. (Choudhry and others, 1979, p. 259-302; Mabey and others, 1982, p. 49-102; Cunningham and others, 1985, p. 409-416; Langford and Carey, 1987, p. 225-239; Cunningham and others, 1988, p. 1090-1097; Fox, 1988, p. 445-467; Cunningham and others, 1985; Pelizzetti and others, 1988, p. 469-497; Zepp, 1988; Cunningham and Goldberg, 1989; Goldberg and others, 1989. It has been found that some compounds which are not rapidly biodegraded and are not lost because of volatility, hydrolysis, or adsorption; have an environmental loss rate that is partly or wholly caused by sunlight photolysis. (Mill and Mabey, 1978, p. 184-213; Zepp and others, 1985, p. 74-81; Zepp, 1987; Zepp and others, 1987, p. 443-450; and Zepp, 1988a, p. 193-214). Experience has taught us that any highly toxic compound of anthropogenic origin that is highly chlorinated must be tested for photolytic degradation if we are to understand its behavior in water and further understand its waterborne transport properties. (Irick and Boyd, 1973, p. 238-241; Ross and Crosby, 1975, p. 242-244; Kiwi and Grätzel, 1982, p.931-939; Mill and Haag, 1986, p. 61-66; Fox, 1988, p. 445-467; and Jardim and Campos, 1988, p. 243-248). Thus, when highly chlorinated materials that are resistant to normal biodegradation pathways are used on a large scale in agricultural areas, such as the midcontinent, it is propitious to test the proclivity of the molecule to be photolytically degraded.

Direct and indirect photolysis mechanisms can act on chlorinated hydrocarbons, (Cunningham and others, 1985, p. 409-416; Cunningham and others, 1988, p.1090-1097; and Goldberg and others, 1989); however, in the case of atrazine found in the Cedar River, indirect photolysis may be of greater importance than direct photolysis in producing photolytic decomposition. This is due to an abundance of nitrate ion which can be readily photoactivated in aqueous solution to produce hydroxyl (.OH) radical (Haag and Hoigné, 1985, p. 1659; Goldberg and others, 1989). This effect, however, is not linear in that a 20-times increase in nitrate ion yields a 7-times increase in steady-state .OH radical concentration.

The purpose of our investigation was to determine the effect of direct sunlight photolysis on the degradation of atrazine as the atrazine in runoff is collected by tributaries and transported to the main stem of the Cedar River. Furthermore, if any significant degree of photolytic degradation takes place, it was within the scope of this study to determine the environmental factors that would exacerbate this process including evaluation of the variables that affect the photolytic degradation process. Complete information about this process should include: the rate of degradation, amount of degradation during residence time in the watercourse, the dependency on environmental factors and the expected half-lives of existence in various locales within the study area.

STUDY SITE

Atrazine, a chlorinated herbicide, is used extensively for herbicide control in the Cedar River drainage basin. The study area, defined by the map in figure 1, shows the Cedar River drainage immediately to the south of Cedar Rapids, Iowa, as it runs between Iowa City and Conesville, Iowa. This drainage basin includes several subbasins and contains streamflow-gaging stations and an extensive network of sampling sites that have been established by the U.S. Geological

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[1] U.S. Geological Survey, Lakewood, Colo.

Survey in Iowa. The Cedar River drains an agricultural basin that is 81 percent cropland, 12 percent forest, and 7 percent other uses. The geology consists of a glacial drift that overlies Devonian and Silurian limestone and dolomite bedrock aquifers; the Cedar River flows on an alluvial aquifer. The alluvial aquifer is a medium-grained quartz sand that includes gravel and some cobbles. Estimated traveltime within the tributaries sampled ranged from 18 hours to 11 days, at the time of sampling. Seepage-run velocities used for calculations in certain parts of this paper were made in the summer of 1989 (P.M. Schulmeyer, U.S. Geological Survey, written commun., 1990).

SAMPLING

Samples were collected at the main stem and in the tributaries of the Cedar River at sampling sites shown in figure 1. Water samples were collected with a DH-48 sampler using a standard equal-discharge-increment sampling method (L.R. Kister and W.B. Garrett, U.S. Geological Survey, written commun., 1983) with 10 sampling increments for the main stem and 3 or 5 increments on the tributaries, depending on the size of the tributary. Samples were stored continuously at 0 to 4°C (degrees Celsius) in the dark until irradiation in the U.S. Geological Survey laboratory in Denver.

ANALYTICAL PROCEDURES

A 455 mL (milliliter) aliquot of each river sample was added to a cylindrical, jacketed, pyrex[3] photolysis cell. Five mL of this aliquot were withdrawn as a blank, 10 mL of an 8.73×10^{-5} M (molar) atrazine solution in water was added to the remaining 450 mL of sample resulting in 460 mL of a 2.0×10^{-6} M atrazine solution.

The unfiltered sample, with added atrazine, was irradiated in a Rayonet-type irradiator with RPR-3600 sunlight lamps emitting in the wavelength range 295 to 400 nm (nanometers). The output incident upon the irradiation cell was measured by means of a ferrioxalate actinometer and was found to be 4×10^{-4} Einsteins per minute. This duplicates the natural sunlight spectrum in the range which

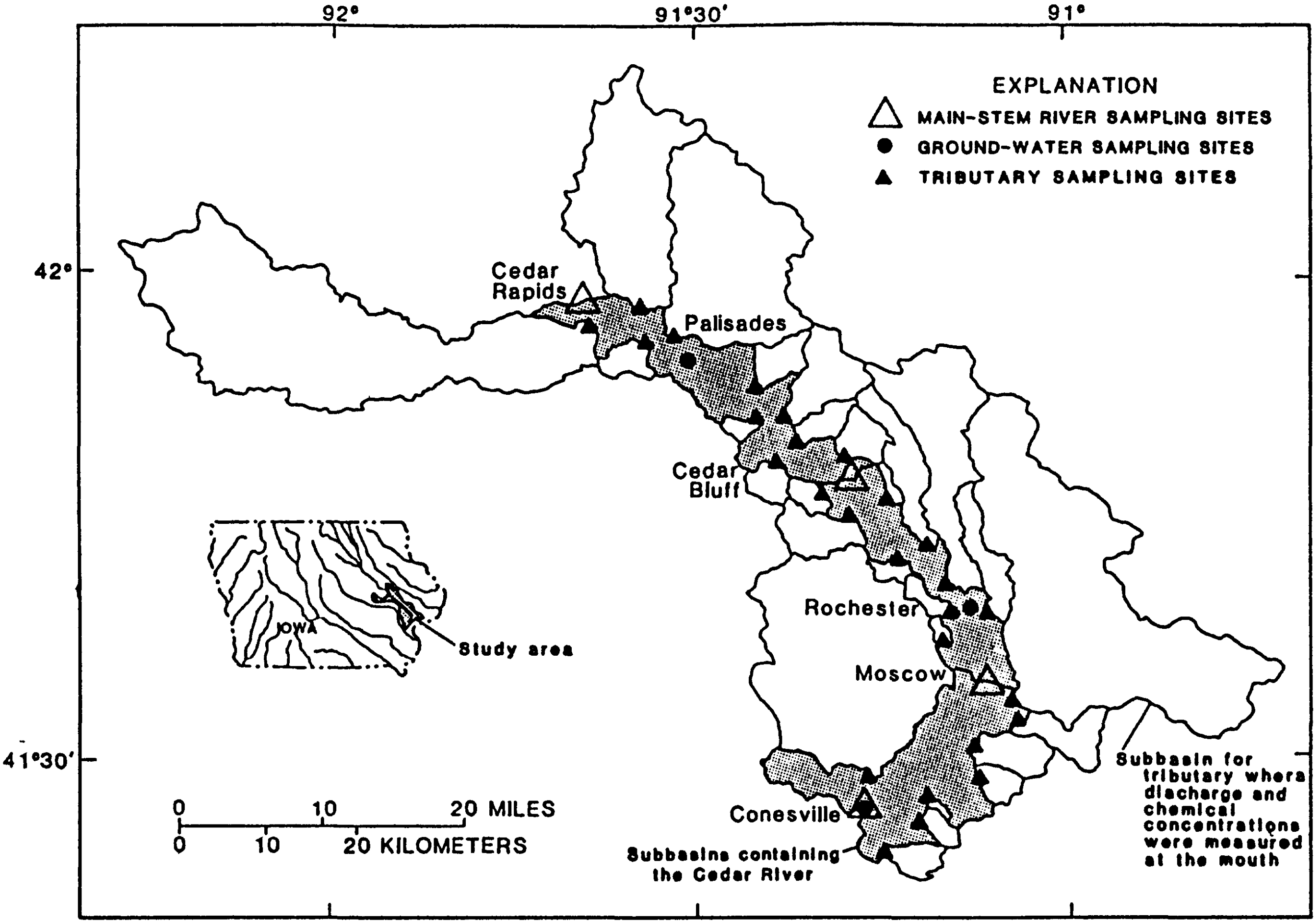
92°
91°30'
91°
42°
41°30'
EXPLANATION
△ MAIN-STEM RIVER SAMPLING SITES
● GROUND-WATER SAMPLING SITES
▲ TRIBUTARY SAMPLING SITES
Cedar Rapids
Palisades
Cedar Bluff
Rochester
Moscow
Conesville
IOWA
Study area
0 10 20 MILES
0 10 20 KILOMETERS
Subbasins containing the Cedar River
Subbasin for tributary where discharge and chemical concentrations were measured at the mouth

Figure 1. Cedar River study area with drainage basins where discharge and chemical concentrations were determined.

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[3] The use of brand, firm, or trade names in this paper is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

produces abiotic photolysis. (Zepp, 1977, p. 359; Zepp and others, 1984, p. 119-125; Zepp, 1987; Zepp, 1988a, p. 193-214; and Zhou and Mopper, 1990, p. 1-18). During irradiation, the temperature in the irradiated sample was maintained at 15 to 18 °C. The sample was continuously stirred during photolysis. A part of the original sample with added atrazine was kept in the dark at room temperature as a control.

During irradiation, the lamp output intensity varied by less than 10 percent, as measured by means of a photodiode-near-UV filter combination (Oriel Corp.). Five mL aliquots of the photolyzed samples and 5 mL aliquots of the control samples were treated identically as soon as they were removed from their containers. The procedure was as follows:

1. Ten percent volume to volume neat acetonitrile was added to minimize adsorption of atrazine onto sample vial walls and to serve as a preservative.
2. The sample with added acetonitrile was filtered through a 1 centimeter 0.45 micrometer, nylon filter under pressure and stored in a refrigerator until it was analyzed. Average storage times were 1 to 2 days.

High Pressure Liquid Chromatography analyses were performed using a mobile phase of 60:40 $CH_3CN:H_2O$ with a flow rate of 1.0 mL per minute. The fluorescence detector was set to an analyzing wavelength of 221 nm (a variation on the method of Tanaka and others, 1981, p. 227-230). The injection volume was 200 microliters and the elution time was 5 minutes. Two injections were made for each sample run resulting in precision in measurement of the peak area of ± 3 percent. The standard calibration plot for atrazine was linear between 2×10^{-7} M and 2.3×10^{-6} M.

RESULTS AND DISCUSSION

The photolysis data for sampling points along nine tributaries and three locations on the main stem are plotted in figure 2 as time of photolytic degradation in hours versus concentration in moles per liter. From this data the half-lives of photolytic decomposition are derived; they ranged from 38 to 330 hours. Different half-lives were obtained for different sample locations. Some sampling sites degraded atrazine at a rapid rate, such that almost all the atrazine was lost in 330 hours, whereas samples from other locations lost only 50 percent of the atrazine in the same 330 hour period. This observation reveals the importance of the sample matrix and highlights the extreme site specificity of photolytic degradation in this river basin.

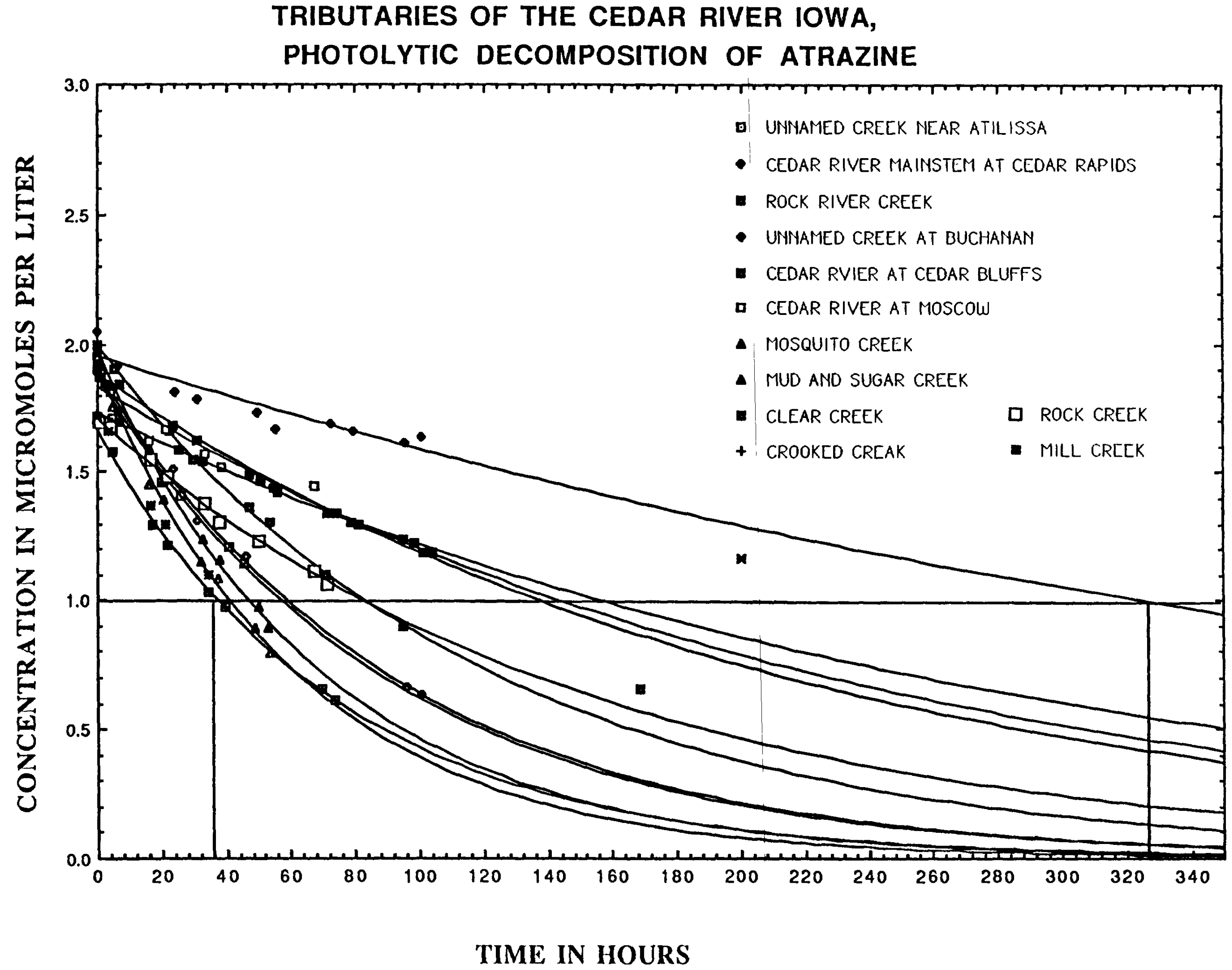


Figure 2. Photolytic decomposition of atrazine in the Cedar River, Iowa, and its tributaries.

Nitrate ions produce hydroxyl radicals in water under direct sunlight irradiation. (Mill and others, 1978, p. 223-236; Mabey and others, 1982, p. 49-102; Haag and Mill, 1987, p. 359-369; Zepp and others, 1987, p.443-450; Goldberg and others, 1989, p. 269-340; and Turchi and Ollis, 1990, p. 178-192). Hydroxyl radicals will attack atrazine and initiate a degradation chain. The main mechanism of attack involves OH replacement of the group in the two position to form hydroxy atrazine. Two alternate oxidation pathways are shown in figure 3 but are of lesser importance. The chain of photolytic degradation products are seen in figure 3, (Pelizzetti and others, 1990, p. 1559-1565). Once degradation is initiated, the time of decomposition of an initial amount of atrazine can be a little as a few minutes. In one study with titanium dioxide as the hydroxyl radical initiater, atrazine concentration was reduced from 2 ppb (parts per billion) to less than 0.1 ppb in 10 minutes. The end product of the degradation chain is cyanuric acid. It is of interest to note that its solubility in water is greater than that of atrazine. One of the byproducts of atrazine decomposition is nitrate. It has been shown that 2 mol (moles) of nitrate ion are formed for every mole of atrazine that is fully degraded. (Pelizzetti, 1990, p. 1559). Reduction of atrazine to the point where two nitrate ions are produced, meaning that two out of five nitrogen (N_2) atoms in the molecule have been degraded, has been accomplished in degradation times between 20 and 75 hours, depending upon the steady-state concentration of hydroxyl radical. Even though the initial degradation of atrazine to the first daughter product in the degradation chain takes place very rapidly, much longer irradiation times are required to photolyze atrazine through all the degradation chain products to the final product. It should be noted that atrazine will not photolytically degrade when irradiated with wavelengths longer than 340 nm.

Using the data obtained from analysis of the degradation of atrazine, it is possible to construct a model that relates the nitrate concentration in the tributary to the half-life of photolytic atrazine degradation. Figure 4 is a graph of the half-life photolysis time in hours as a function of the concentration of nitrate in a tributary, in moles per liter times 10^6. By fitting a curve to this data, and finding the equation of the curve, it is possible to calculate the half-life of degradation for any of the tributaries listed, assuming that the only reactive factor other than sunlight is nitrate. The model equation for this calculation is

$$X=10^{\left\{\frac{-\log\left(\frac{y}{8361}\right)}{2.01}\right\}} \tag{1}$$

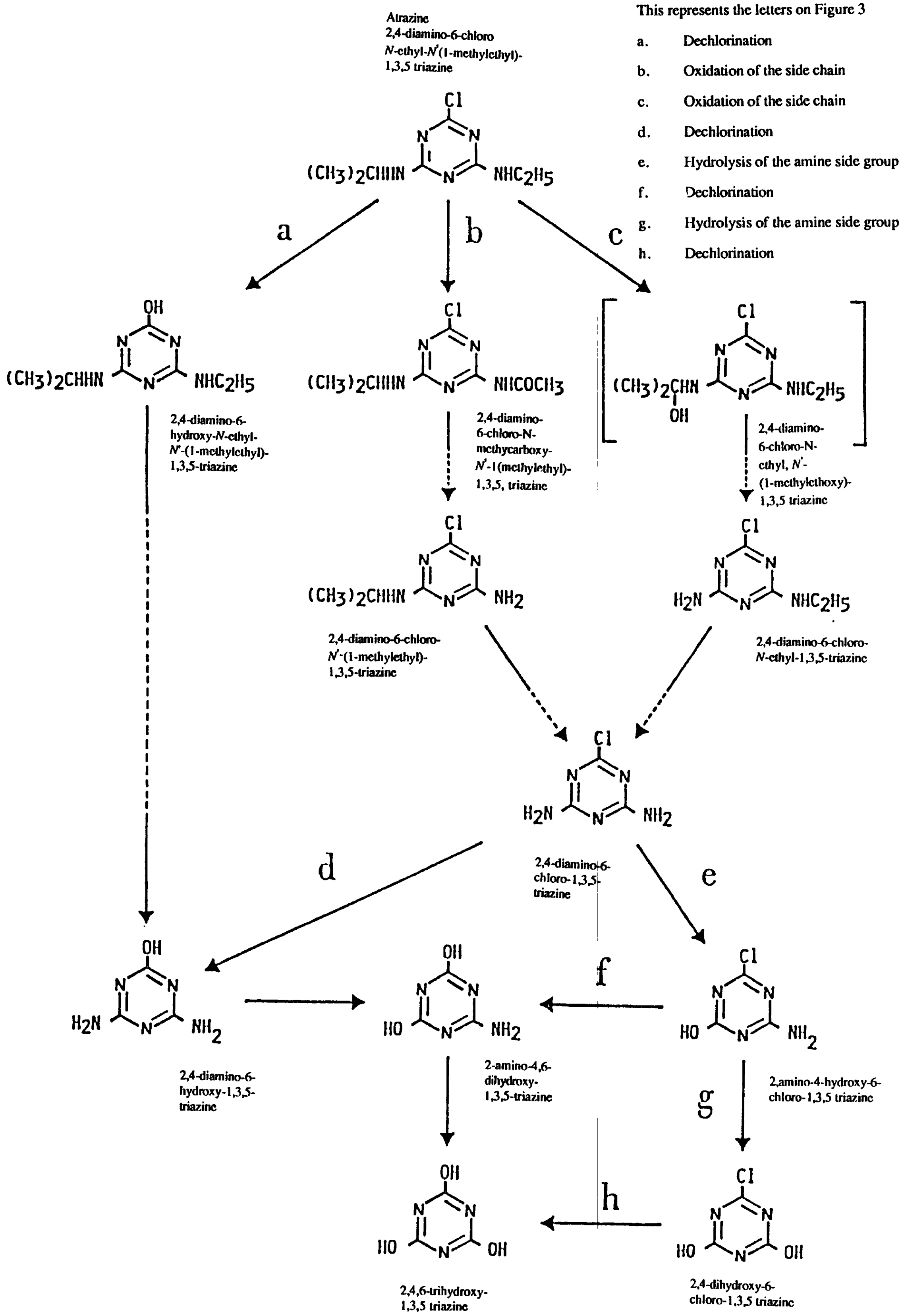
where X = the photolytic half-life, in hours, and
y = the nitrate concentration, in millimoles.

Table 1 is a listing of sample sites where nitrate concentrations have been measured. Equation 1 was used to calculate the values of the half-lives of atrazine degradation at these sites. The calculated half-lives in the sampled tributaries were compared to the measured half-lives at these sites and agreed within 20 percent. The model from which equation 1 is derived employs two variables which are: (1) the number of incident photons impinging on the atrazine in solution in the tributary, and (2) the concentration of nitrate ions in the tributary.

From a practical standpoint it would be useful to know the amount of atrazine that was photolytically degraded during the time of travel in the tributary. A calculation of this sort requires some amount of approximation. Based on existing data, it is necessary to estimate the length of the tributary. With this estimate, and the value of the water velocity in the tributary, one can then estimate a time of travel. Assuming that atrazine enters the tributaries at given points which are chosen as representative injection points, then figure 5 displays the percentage of photolytic degradation that occurs, during time of travel, in the listed tributaries of the Cedar River. In calculating this data a most conservative viewpoint was taken wherein the variables of photon flux and time of travel were minimal values. The degradation percentages listed here are probably smaller than one would find if a more accurate time-of-travel measurement could be made.

Figure 5 illustrates that in some tributaries of the Cedar River, the amount of photolytic degradation that occurs during the time of transport from the tributary to the river is of significant interest as the values are greater than 50 percent. In other tributaries the amount of degradation is rather small and amounts to only a few percent. These data verify the premise that atrazine is degraded by photolysis in the tributaries of the Cedar River and that a complete mass balance would require an awareness of this effect. A salient point made by this study is that any discussion of the transport of atrazine from land runoff to the main stem of the Cedar River must also take into account losses incurred by photolytic degradation.

In the main stem of the Cedar River, the nitrate concentration is very low. Indeed, most of the analyses of nitrate are below detectable limits. This correlates with the very small amount of atrazine degradation found in samples taken from the main stem. Two environmental circumstances act to mitigate the photolytic effect in the main stem of the river. The first factor is the comparatively large amount of photon absorption and scattering in the main stem because of the presence of more suspended sediment and more light absorbing compounds in the water. This comparison of conditions between the tributaries and the main stem does not necessarily hold true for all the tributaries, but it is true on the average. Secondly, the extremely low concentration of nitrate in the Cedar River main stem does not provide very much nitrate to act as the sensitizer to produce .OH radicals. There may be other sources of .OH radical sensitizers in the river; nevertheless, the small amount of atrazine degradation found in the river seems to corroborate the supposition that nitrate is the only sensitizer that produces reasonably large amounts of .OH radical when the system is exposed to sunlight. The premise that the hydroxyl radical is the species that is responsible for atrazine degradation in the tributaries seems to be supported by this circumstance.



Atrazine
2,4-diamino-6-chloro N-ethyl-N'(1-methylethyl)-1,3,5 triazine
a
b
c
2,4-diamino-6-hydroxy-N-ethyl-N'-(1-methylethyl)-1,3,5-triazine
2,4-diamino-6-chloro-N-methycarboxy-N'-1(methylethyl)-1,3,5, triazine
2,4-diamino-6-chloro-N-ethyl, N'-(1-methylethoxy)-1,3,5 triazine
2,4-diamino-6-chloro-N'-(1-methylethyl)-1,3,5-triazine
2,4-diamino-6-chloro-N-ethyl-1,3,5-triazine
2,4-diamino-6-chloro-1,3,5-triazine
d
e
f
g
h
2,4-diamino-6-hydroxy-1,3,5-triazine
2-amino-4,6-dihydroxy-1,3,5-triazine
2,amino-4-hydroxy-6-chloro-1,3,5 triazine
2,4,6-trihydroxy-1,3,5 triazine
2,4-dihydroxy-6-chloro-1,3,5 triazine

This represents the letters on Figure 3

a.	Dechlorination
b.	Oxidation of the side chain
c.	Oxidation of the side chain
d.	Dechlorination
e.	Hydrolysis of the amine side group
f.	Dechlorination
g.	Hydrolysis of the amine side group
h.	Dechlorination

Figure 3. Photolytic degradation chain of s-atrazine. Reprinted from Environmental Science and Technology, v. 24, p. 1560. Copyright 1990, American Chemical Society, and published with permission.

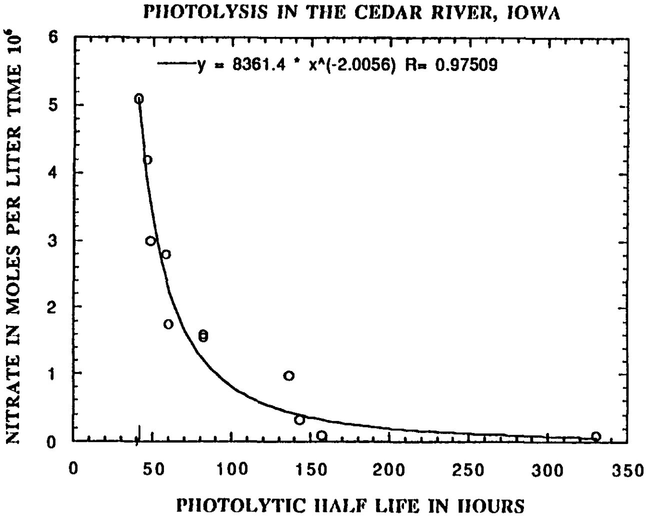


Figure 4. Nitrate concentration, in millimoles per liter, as a function of photolytic half-life, in hours.

CONCLUSIONS

Abiotic degradation of atrazine occurs in both the Cedar River, Iowa, and in tributaries to the Cedar River; however, the amount of degradation is extremely site specific. In the Cedar River itself, there is only a few percent decomposition during traveltime in the river from Cedar Rapids, Iowa, to Conesville. The amount of degradation in the tributaries of the Cedar River varies from a few percent to slightly more than 50 percent during time of travel from selected entrance points to the main stem of the river. Specific degradation half-lives for the tributaries sampled ranged from 33 to 330 hours. This iterates the site specificity of photolytic degradation. The amount of degradation correlates directly with the concentration of nitrate ion at the sampling point. The explanation for this is that sunlight reacts mechanistically with nitrate to form .OH radical. The radical then reacts with atrazine beginning the degradation chain. Several products are formed as atrazine goes through the degradation chain and the

Table 1. *Calculation of the atrazine photolytic half-life for all sample stations on the Cedar River, Iowa*

Location	Nitrate concentration	Date	Calculated atrazine half-life, in hours
Cedar River at Cedar Rapids	0.10	9/20/89	285
Cedar River at Cedar Rapids	.10	9-21-89	285
Cedar River at Moscow	.10	9-21-89	285
Cedar River at Conesville	.10	9-21-89	285
Cedar River at Conesville	.10	9-22-89	285
Cedar River at Conesville	.13	9-20-89	250
Cedar River at Moscow	.21	9-20-89	197
Cedar River at Cedar Bluffs	.23	9-21-89	188
Cedar River at Cedar Bluffs	.26	9-21-89	177
Cedar River at Cedar Bluffs	.32	9-21-89	159a
Cedar River at Cedar Bluffs	.33	9-20-89	157
Cedar River at Conesville	.33	9-20-89	157
Cedar River at Cedar Bluffs	.34	9-21-89	155
Indian Creek	.40	9-20-89	143
Cedar River at Cedar Rapids	.63	9-20-89	114
Clear Creek	.71	9-20-89	107
Big Creek	.92	9-20-89	94
Clear Creek	.98	9-20-89	91
Sugar Creek Tributary	1.10	9-21-89	86
Gower Creek	1.50	9-20-89	74
Cedar River at Palisades	1.60	9-19-89	71
Unnamed Creek	1.60	9-21-89	71
Rock Creek	1.60	9-21-89	71
Cedar River at Palisades	1.70	9-18-89	69
Coon Creek	1.70	9-20-89	69
Smith Run	1.70	9-21-89	69
Unnamed Creek	1.90	9-21-89	66
Crane Creek	2.00	9-21-89	64
Baldwin Creek	2.60	9-20-89	56
Mill Creek	2.60	9-20-89	56
Pee Dee Creek	2.60	9-20-89	56
Nickolson Creek	2.70	9-21-89	55

Table 1. *Calculation of the atrazine photolytic half-life for all sample stations on the Cedar River, Iowa--Continued*

Location	Nitrate concentration	Date	Calculated atrazine half-life, in hours
Little Mosquito Creek	2.80	9-21-89	54
Rock Run	3.00	9-21-89	52
Sugar Creek Tributary	3.10	9-21-89	51
Spring Creek	3.60	9-20-89	48
Prairie Creek	4.20	9-20-89	44
Clear Creek Tributary	4.20	9-20-89	44
Crooked Creek	4.20	9-22-89	44
Sugar Creek	4.40	9-21-89	43
Sugar Creek	5.10	9-21-89	40
Sugar Creek Tributary	5.90	9-21-89	37
Wapsinoic Creek	7.60	9-22-89	33

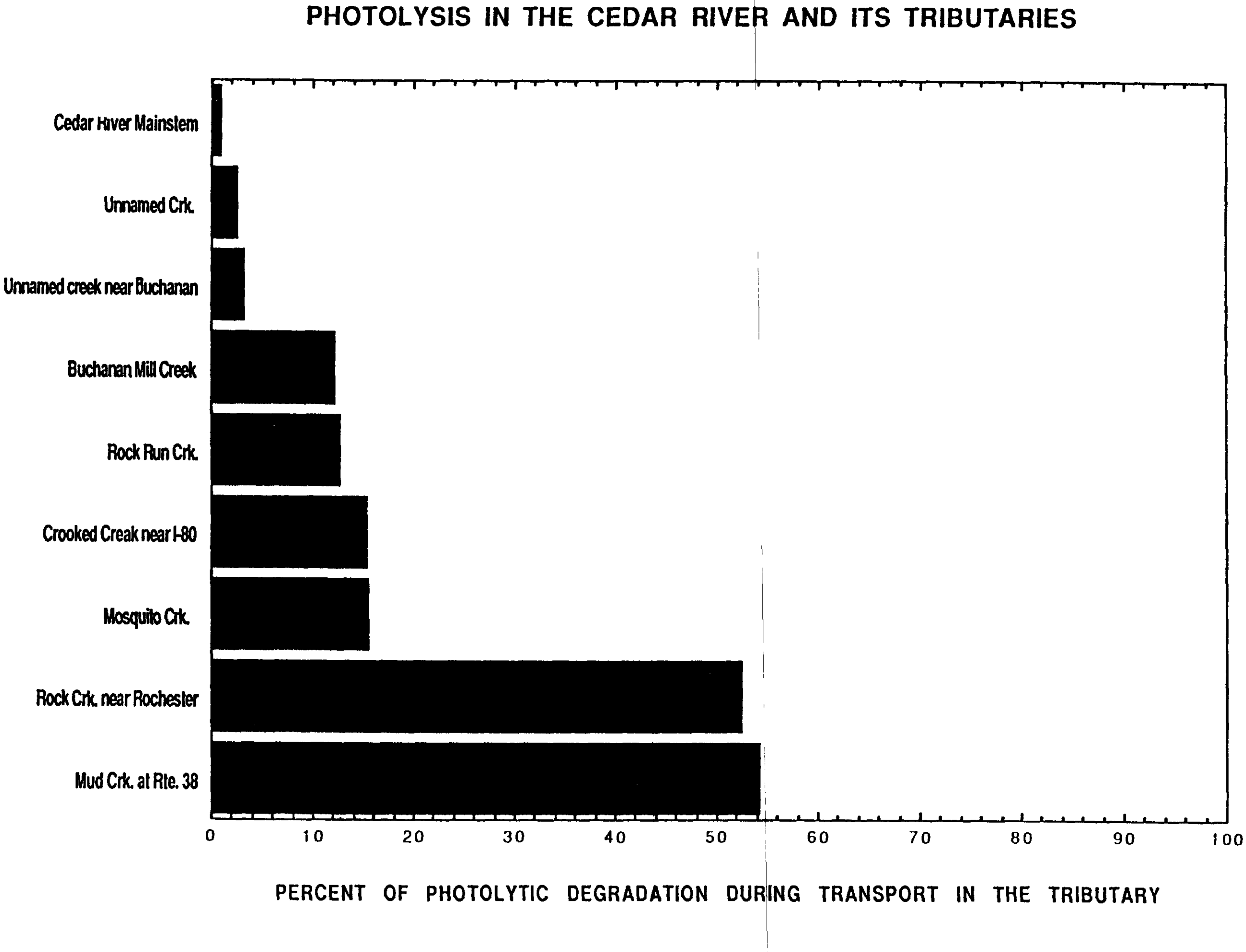


Figure 5. Percentage of abiotic, photolytic degradation of atrazine during travel time in tributaries of the Cedar River, Iowa.

consequence of the presence of these compounds may be of equal interest to that of atrazine itself inasmuch as each product may have specific environmental effects and many of the products are more water soluble than atrazine. Because nitrate concentrations in the tributaries result mainly from the agricultural practices in the region, one would expect the photolytic degradation rates of atrazine to vary seasonally in direct relation to the amount of nitrate present in the tributaries. The main stem of the Cedar River has a very low nitrate concentration, thus, there is relatively little abiotic photolysis of atrazine once the material has been deposited in the main stem. The tributaries offer a hydrologic setting that results in larger amounts of degradation.

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PLANNED STUDIES OF MOVEMENT OF NITROGEN SPECIES AND HERBICIDES ON CLAYPAN SOILS AT THE MANAGEMENT SYSTEMS EVALUATION AREA IN MISSOURI

By Dale W. Blevins[1]

ABSTRACT

Numerous studies of nitrogen, atrazine, and alachlor are being started by the U.S. Department of Agriculture and the U.S. Geological Survey at the Goodwater Creek basin in north-central Missouri. Claypan soils, loess, and glacial drift cover most of the basin. The primary crops are soybeans, corn, pasture, and wheat. Ground-water, surface-water, and water-quality data will be collected from study areas of 0.022, 1, 20 to 60, 3,200, 7,040, and 17,900 acres.

The large clay content of surficial materials in the basin permits macropore flow and provides an opportunity to conduct solute-transport studies. Other studies will determine the effects of three crop-management systems on the fate and transport of nitrogen species, alachlor, and atrazine. The U.S. Geological Survey will study the use of nitrogen and oxygen isotopes to trace nitrate from fertilizer through the unsaturated and saturated zones. Techniques to significantly decrease the cost of analyzing for nitrogen isotope ratios and to analyze oxygen-isotope ratios in nitrate will be developed.

INTRODUCTION

Five study sites in the Midwest have been selected by the U.S. Department of Agriculture (USDA) and the U.S. Geological Survey (USGS) for intensive study of water quality associated with agricultural activities. These sites have been designated Management Systems Evaluation Areas (MSEA). The site in north-central Missouri was chosen primarily because the claypan soils that cover the site represent large parts of the Midwestern United States (fig. 1). This paper describes the study area and some of the USDA and USGS studies planned for the Missouri site.

DESCRIPTION OF STUDY AREA

The Missouri MSEA is in the Goodwater Creek basin near Centralia (fig. 1), which has been instrumented by the Agricultural Research Service for 17 years to measure runoff, nitrate concentrations in streams, ground-water levels, rainfall, and several other meteorological conditions.

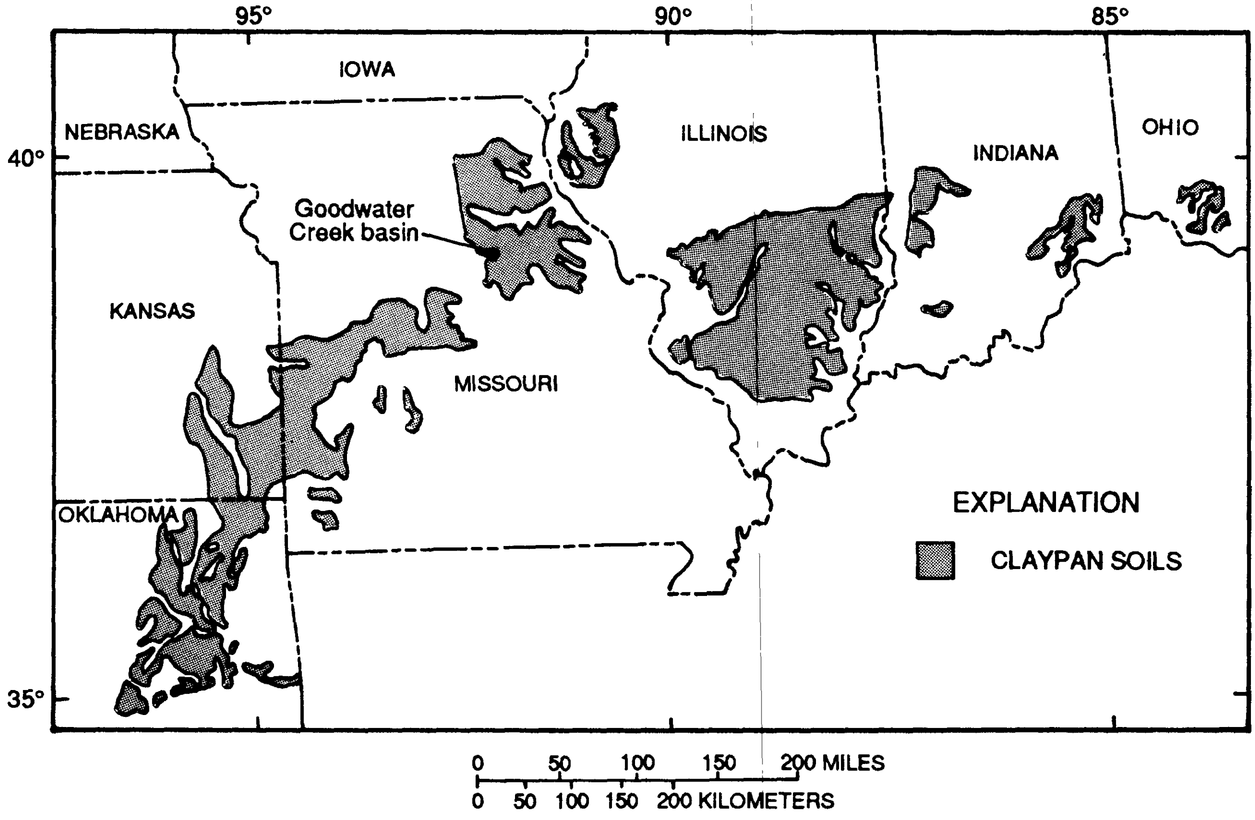

Figure 1. Location of Goodwater Creek basin, Missouri, and claypan soils in the Midwestern states (modified from Smith and others, 1979, p. 3).

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[1] U.S. Geological Survey, Independence, Mo.

The three existing streamflow gages in the basin measure flow from drainage areas of 5, 11, and 28-square miles. Claypan subsoils in the Goodwater Creek basin are classified as slowly permeable, but considerable water may percolate through the clay layer because flat topography prevents rapid runoff and shrinking of the clay materials during dry periods causes the subsoil to fracture, permitting macropore flow. The primary crops are soybeans, corn, pasture, and wheat.

The hydrogeology of the Goodwater Creek basin has been described in detail by Hesemann (1979). Generally, 0 to 16 in. (inches) of silt loam overlie a 3-ft (foot)-thick claypan. The topsoil and the upper part of the claypan are naturally acidic and low in nutrients. The claypan formed on as much as 10 ft of Wisconsinan-age loess. The principal clay minerals of the claypan layer are of the montmorillonite group and are subject to large changes in volume with changes in moisture content. The loess overlies about 40 ft of glacial drift. The drift is largely composed of silty clay with sporadic sand lenses of limited areal extent. The sand lenses differ in thickness from 1.6 to 8.2 ft. Hydraulic heads in the glacial drift generally range from 1 to 10 ft below the land surface. Barometric efficiencies computed for observation wells indicate that the claypan confines water in the glacial drift during wet periods. Flow directions are downward and away from the hilltops, horizontally toward the streams, and upward underneath the streams. Bedrock consists of Pennsylvanian limestone and shale and perhaps the top of the Burlington Limestone of Mississippian age.

Samples were collected from six wells less than 125 ft deep in and near the study area and analyzed for nitrate concentrations in a recent rural well survey. The average nitrate concentration of these samples was three times the Environmental Protection Agency drinking water standard of 10 milligrams per liter as nitrogen (N); (Sievers and Fulhage, 1989).

MONITORING ACTIVITIES

The USDA and the USGS installed 30 wells in 9 nests throughout the Goodwater Creek basin during the summer of 1990. These wells will be sampled to determine baseline concentrations of dissolved nitrate, nitrite, alachlor, ammonium, and atrazine in ground water underlying the Goodwater Creek basin. The three streamflow gages will be upgraded with automatic samplers and possibly water-quality monitors.

Three field-size (20 - 60 acres) and thirty 1-acre plots have also been established on the Goodwater Creek basin for smaller scale studies. The three field-size plots will be intensely instrumented to measure and sample ground water and surface runoff. Monitoring activities in the 1-acre plots will differ depending on the specific research projects that will use the plots. Also, a nearby experimental farm contains forty-one 0.022-acre plots that have been used since 1941 for erosion and crop studies. These plots are outside the Goodwater Creek basin but are already instrumented to measure runoff and sediment yields and will be used in conjunction with the plots in the Goodwater Creek basin.

The crop rotations on most plots will be corn and soybeans with large fertilizer and herbicide inputs; sorghum and soybeans with medium fertilizer and herbicide inputs; and corn, soybeans, and wheat with low fertilizer and herbicide inputs. All chemical inputs will be accurately measured.

Access to ground water at each of the field-sized plots will be provided by a network of monitoring wells. Well nests, tile drains, and soil-zone lysimeters will be used to collect water samples. Five well nests will be installed at each plot and will consist of four wells. The deepest well will be just above the bedrock glacial drift contact and one well will be 10 ft above, or in, a sand lens, if present. Two more wells will be located to span the expected fluctuation in the potentiometric surface. These well nests will be used to measure vertical head gradients. Each well will have its own sampling equipment to minimize cross contamination. The tile drains will be located just above the claypan to collect water samples from the topsoil after storm events.

Soil cores will be collected at the time of drilling from the land surface to bedrock at each well nest for physical and geochemical analyses. Periodically, soil cores will be analyzed to determine the movement and speciation of nitrogen at different depths in the soil zone.

U.S. DEPARTMENT OF AGRICULTURAL STUDIES

Most of the USDA studies will focus on "monotreated" field- and plot-sized areas. The overall objective of USDA studies is to determine the effects of various farming systems on ground- and surface-water-quality. However, process-oriented studies also are being designed by USDA researchers to fulfill the following objectives:

1. Evaluate the effects of basic soil processes on macropore development and water flow.
2. Determine the effects of basic soil processes on pesticide fate and transport.
3. Determine the effects of a claypan on herbicide and dissolved-nitrogen-species fate and transport in the upper root zone (0- to 10-in. depth).
4. Determine the effects of riparian zones on herbicide and dissolved-nitrogen-species fate and transport.
5. Determine the differences in concentrations of agricultural chemicals in both ground and surface water from small and large basins and identify major processes responsible for the differences.
6. Evaluate selected water-quality models to verify the reasonableness of model output and validate the accuracy of model predictions relative to measured values for claypan soils.
7. Improve the accuracy of model predictions by refining existing components or developing new components that represent processes not currently modeled.
8. Develop model components that predict macropore flow as affected by wetting and drying, freezing and thawing, and other basic soil processes.

U.S. GEOLOGICAL SURVEY STUDIES

Two USGS studies, funded by the Toxic Substances Program, have been started--

1. Macropore flow and transport of agricultural chemicals.
2. Use of nitrogen (^{15}N) and oxygen (^{18}O) isotopes to measure nitrogen cycle processes in claypan soils and glacial-drift aquifers.

The macropore study is in the planning stage and detailed objectives have not yet been developed. However, objectives and preliminary plans for the isotope study are complete. These objectives include—

1. Determine the quantity of dissolved nitrate in ground water from nitrate fertilizers spiked with ^{15}N.
2. Determine the quantity of dissolved nitrate in ground water from nitrate fertilizers using oxygen isotopes in nitrate.
3. Test and refine new methods for isolation and analysis of oxygen isotopes in nitrate.
4. Develop and refine field methods for concentrating nitrate in water samples for nitrogen isotopic analysis.
5. Determine the quantity of nitrate fertilizer lost to surface runoff using ^{15}N-spiked fertilizer and oxygen isotopes in nitrate.

The completion of objectives 3 and 4 will significantly decrease the cost of ^{15}N analyses and allow ^{18}O in nitrate to be used as a tool in many geochemical studies of nitrogen.

SUMMARY

Numerous studies of nitrogen, atrazine, and alachlor are being initiated by the USDA and the USGS at the Goodwater Creek basin in north-central Missouri. Claypan soils, loess, and glacial drift cover most of the basin. The primary crops are soybeans, corn, pasture, and wheat. Ground-water, surface-water, and water-quality data will be collected from study areas of 0.022, 1, 20 to 60, 3,200, 7,040, and 17,900 acres.

The large clay content of surficial materials in the basin permits macropore flow and provides an opportunity to conduct solute-transport studies. Other studies will determine the effects of three crop-management systems on the fate and transport of nitrogen species, alachlor, and atrazine. The USGS will study the use of nitrogen and oxygen isotopes to trace nitrate from fertilizer through the unsaturated and saturated zones. Techniques to significantly decrease the cost of analyzing for nitrogen isotope ratios and to analyze oxygen isotope ratios in nitrate will be developed.

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AN INVESTIGATION OF THE TRANSPORT AND MICROBIAL DEGRADATION OF HYDROCARBONS IN THE SUBSURFACE AT A GASOLINE-SPILL SITE IN GALLOWAY TOWNSHIP, NEW JERSEY

By Jeffrey M. Fischer[1], Arthur Baehr[1], and Nicholas P. Smith[1]

ABSTRACT

A unified study of the transport and microbial degradation of hydrocarbons is being conducted at a gasoline spill site in Galloway Township, New Jersey. The composition of unsaturated zone vapors and shallow ground-water quality are being investigated by using an areally and vertically intensive monitoring network. Microbial activity is being analyzed in sediment samples. Field experiments are being conducted to determine parameters for mathematical transport models. Laboratory experiments have been conducted to isolate phenomena to rigorously test submodel hypotheses. The goal of the project is to integrate results of field and laboratory investigations into mathematical models of the transport and fate of hydrocarbons in the subsurface under natural conditions and during site remediation. The findings of the field, laboratory, and modeling investigations are expected to be transferable to other contaminated sites.

INTRODUCTION

Gasoline spills from leaking underground storage tanks and pipelines pose a threat to ground-water quality. Gasoline is almost entirely a mixture of hydrocarbons. In the subsurface, a hydrocarbon constituent of gasoline, such as benzene, can be transported as a solute or vapor in addition to bulk gasoline movement (fig. 1). Microbial degradation of hydrocarbons in the subsurface also can be significant. Quantifying the transport of such a contaminant under natural conditions and during site remediation is a multiphase, compositional, and reactive problem. A research program that addresses this problem must include field, laboratory, and modeling components.

The major objectives of the Galloway project are the development of data-collection methods for pathway quantification and the development of mathematical models of the transport and fate of hydrocarbons in the subsurface.

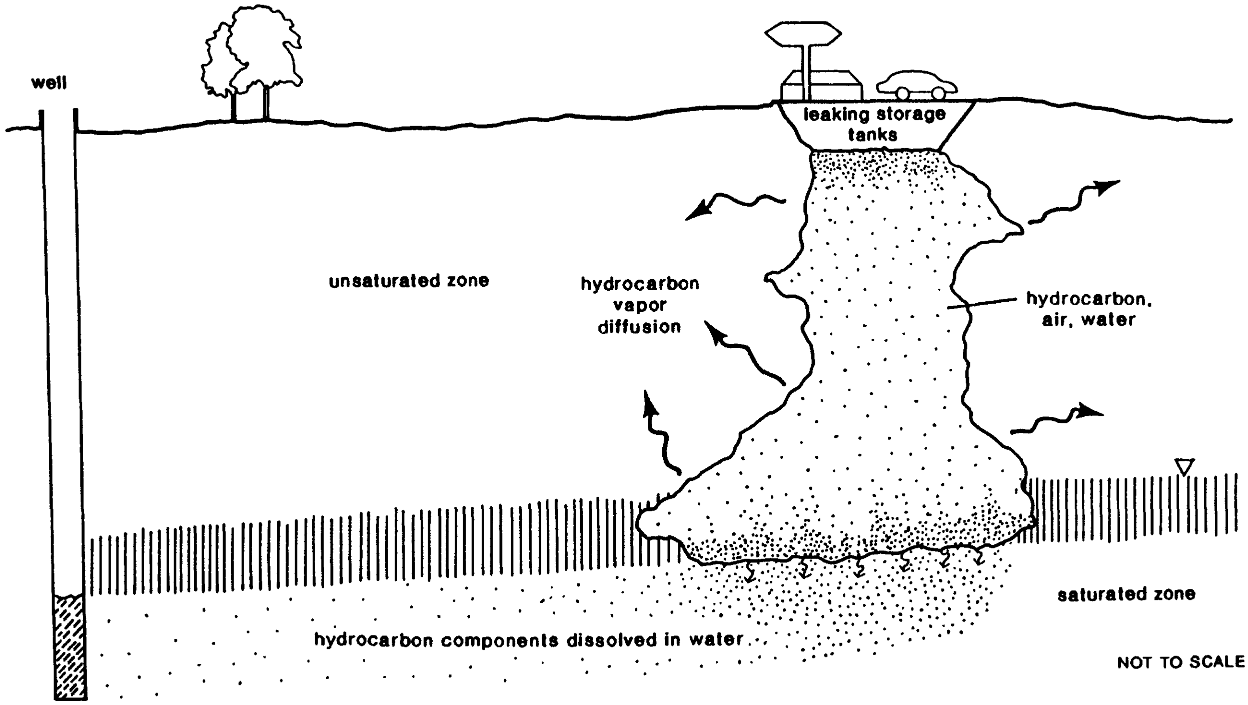

Figure 1. Transport of spilled hydrocarbons in the subsurface under natural conditions.

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[1] U.S. Geological Survey, West Trenton, N.J.

Hydrocarbon contaminants introduced to the unsaturated zone and shallow ground water can enter the atmosphere through volatilization at the ground surface, degrade to simpler molecules by microbial processes in the unsaturated zone, or be transported into an aquifer system as solutes which potentially threaten water resources. A program is being developed to collect data at the appropriate physical scales required to determine the mass flux associated with each pathway. The objective of this exercise is to derive transfer value in the form of data-collection methods that can be applied at other sites where the subsurface is contaminated by hydrocarbons.

Mathematical models are required to transform data into predictions of contaminant transport and fate. Models are being developed to simulate hydrocarbon transport and degradation under natural conditions and where advective air-phase transport is induced by venting wells. These models will be used to evaluate hydrocarbon-contaminated sites and to design optimal venting installations for site remediation. A discussion of the design application for venting transport models is presented by Welty and others (1991, this Proceedings).

This paper describes the investigations that comprise the Galloway project. The project work plan includes field studies, laboratory experiments, and mathematical model development. The interdisciplinary program encompasses the work of 16 investigators--nine from the U.S. Geological Survey (USGS) and seven from three universities. Table 1 provides a list of these investigators and a brief description of their activities.

Table 1. *Investigators contributing to the Galloway research project*

U.S. Geological Survey, West Trenton, N.J.	
Arthur L. Baehr Jeffrey M. Fischer Ronald J. Baker Matthew A. Lahvis Nichnolas P. Smith Jacob Gibs	Program coordination, site hydrogeology, instrumentation, unsaturated-zone vapor analysis, *in-situ* estimates of microbial degradation, laboratory experiments of hydrocarbon diffusion and microbial degradation, venting remediation, mathematical-model development
U.S. Geological Survey, National Research Program, Reston, Va.	
Mary Jo Baedecker Isabelle M. Cozzarelli Curtis S. Phinney	Shallow ground-water analysis, geochemistry and microbiology
Drexel University, Philadelphia, Pa.	
Claire Welty Craig J. Joss Jonathan J. Dillow	Air flow and induced hydrocarbon-transport modeling, coupled transport and optimization modeling
University of Virginia, Charlotsville, Va.	
Aaron L. Mills Susan E. Randall	Microbial analysis of sediments
University of Lowell, Lowell Mass.	
Clifford J. Bruell Craig D. Gilbert	Dense-vapor laboratory experiments

SITE HISTORY

In October 1987, the USGS initiated a project in cooperation with the New Jersey Department of Environmental Protection (NJDEP) to study the transport of hydrocarbons associated with a remediation technique commonly referred to as induced venting. Induced venting involves the withdrawal of air through wells screened in the unsaturated zone (fig. 2). This remediation scheme causes hydrocarbon contaminant mass to be reduced through enhanced volatilization.

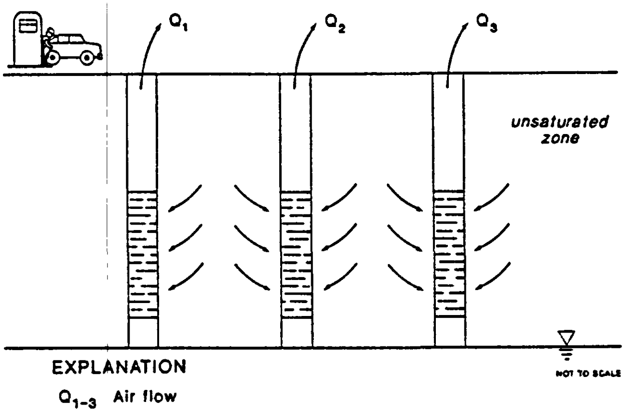

Figure 2. Schematic drawing of the induced venting method for remediating subsurface soils.

Gasoline leaking from a single storage tank located on a farm in Galloway Township, N.J., caused a shallow domestic well to become contaminated. The spill was chosen in December 1987 as a research site because a preliminary survey of unsaturated-zone gases indicated that contamination could be mapped areally, which is considered a prerequisite for meaningful study of unsaturated-zone transport. Because the investigation includes a site-remediation plan, the landowners' cooperation was interpreted by NJDEP as a good-faith effort toward site remediation. The site is located in the Green Bank quadrangle about 10 miles west of Atlantic City, N.J. (fig. 3). The site overlies the Cohansey Sand part of the Kirkwood-Cohansey aquifer system. Perched water is found locally in the system (Zapecza, 1989).

When initial subsurface instrumentation was installed (autumn, 1988), it became clear that the site afforded a unique opportunity to study the transport and microbial degradation of hydrocarbons in the unsaturated zone and in shallow ground water under natural conditions. Thus, the project scope expanded to include an increased data-collection program before remediation began, and the period allocated to assess preventing baseline conditions was extended. In April 1989, this site was recognized by the USGS Ground-Water Toxic-Substances Hydrology Program as a site for field research of hydrocarbon fate and transport.

MONITORING NETWORK

The monitoring network at the Galloway site (fig. 4) consists of 27 nests of vapor probes, 8 ground-water observation wells, 2 multilevel ground-water samplers, 5

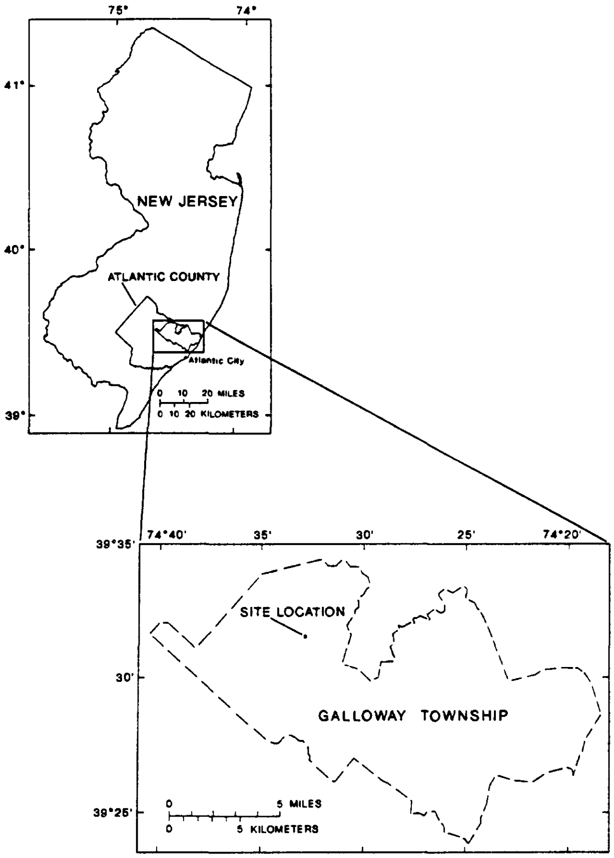

Figure 3. Location of the research sites, Galloway Township, New Jersey.

vapor extraction wells, 2 neutron-probe access pipes, a nest of thermistors, and 5 ground-water-sampling wells installed by NJDEP prior to our investigations.

Vapor probe nests consist of bundles of 0.25-in. (inch) outer- diameter stainless steel tubes, each slotted over a 6-in. length at the end of the tube and placed in a 4-in.-diameter augered hole at the desired depth. Holes for the most part were hand augered. For probes emplaced deeper than 15 ft (feet), a power auger was used to drill the hole. Clean sand was placed around the slotted part of each probe, and bentonite seals were placed between the sand intervals to prevent transport between probes through the augered hole (fig. 5). Vertical distance between probes is as close as 2 ft. Currently (December 1990), 135 vapor probes are installed in 27 nests. The deepest vapor probes were installed at a depth of 22 ft, during the dry summer of 1988 when the water table was low. Water perched above a unit consisting of dense clay stringers at a depth of about 15 ft and extending areally over most of the site has submerged many of the vapor probes. From the submerged probes, perched ground-water samples are collected over the site at small vertical intervals. From unsubmerged probes, vapor samples and air pressures are obtained. Figure 6 illustrates the relations among submerged probes, perched water, and site geology for a vertical section through probe locations 8, 9, and 10. Sediment logs describing the site geology were obtained during the installation of each nest and ground-water-sampling location.

Ground-water samples are obtained from the USGS and NJDEP ground-water-observation wells and 2 multilevel samplers. The 2-in.- diameter USGS observation wells were installed in April 1989 with an 8-in.-diameter hollow-stemmed auger. Stainless-steel casing was used and each USGS well has a 2-ft-long stainless-steel screened interval. Six of the USGS observation wells were installed in three pairs. Wells in each pair were screened over consecutive 2-ft intervals just below the water table. Two multilevel samplers, which allow detailed sampling over a 5-ft depth, were installed in May 1990. The multilevel samplers were driven to a depth just below the water table. The design of these samplers is described by Gibs and others (1991, this Proceedings).

Five stainless steel, 2-in.-diameter vapor-extraction wells were installed in May 1990. These wells were installed with an 8-in. outer-diameter hollow-stemmed auger. Two wells were screened in the unsaturated zone just above the perched water. Each of these wells was paired with a well screened over an interval submerged in perched ground water at the time of installation. This design will allow for a more effective venting remediation if the perched water levels drop below the depth of the lower placed screens. The fifth vapor-extraction well was installed between the perched water and the regional water table. During venting remediation, the amount of hydrocarbons withdrawn from the vapor-extraction wells will be monitored and the mass of hydrocarbon vapors removed will be estimated.

The two neutron-probe access pipes consist of 2.5-in.-diameter steel pipe installed to a depth of 20 ft. A neutron probe can be lowered through the pipe to measure the moisture content of the unsaturated zone. A nest of thermistors was installed to measure subsurface temperatures. Thermistors are placed at 1-ft intervals from land surface to 23 ft below land surface. Wires connecting the thermistors to land surface allow for recording the vertical temperature profile with an ohmmeter.

UNSATURATED-ZONE-VAPOR ANALYSIS

The distribution of gases in the unsaturated zone and the use of these data to estimate hydrocarbon degradation rates by applying a mathematical transport model is discussed by Baehr and others (1991, this Proceedings). Dedicated analytical instruments in the field laboratory installed at the site are used to analyze vapor samples to determine the distribution of gases in the unsaturated zone. A Tracor 540[2] gas chromatograph (GC) is used to measure the concentrations of selected hydrocarbon vapors as well as other gases, such as oxygen, nitrogen, carbon dioxide, and methane. The instrument separates hydrocarbons and methane with a capillary column and detects the vapors with a Flame Ionization Detector (FID). The other gases, and methane, are separated with a carbopack column and detected with a thermal conductivity detector (TCD). A PE Nelson data system is used to store the chromatograph on a personal computer. Compounds are identified on the basis of retention time, and quantified on the basis of peak area. These analytical methods are reported by Baker and others (1991, this Proceedings). A Dohrmann total organic carbon

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[2] Use of trade names in this paper are for identification only and does not constitute an endorsement by the U.S. Geological Survey.

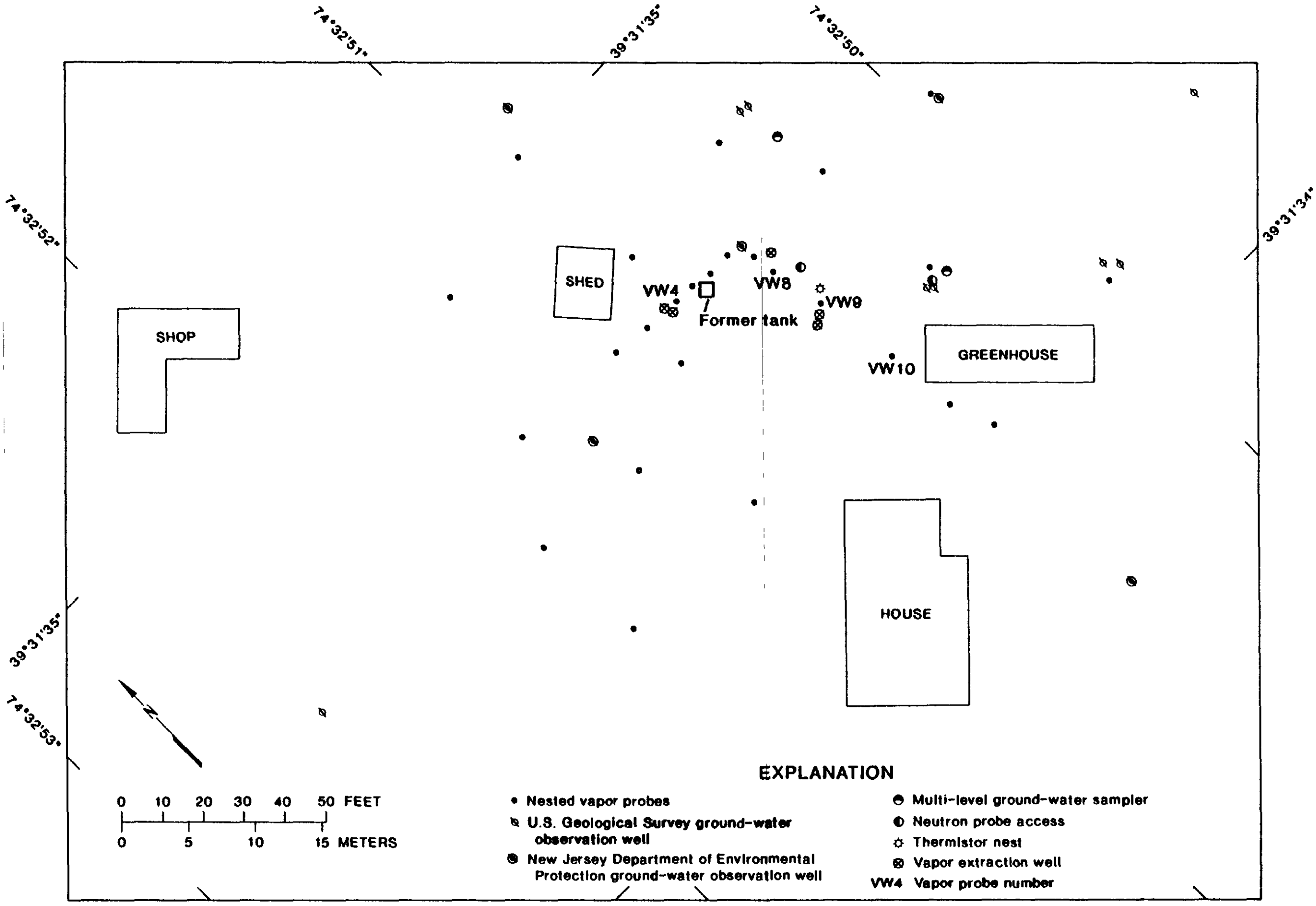
74°32'51"
39°31'35"
74°32'50"
74°32'52"
39°31'34"
39°31'35"
74°32'53"
SHOP
SHED
VW4
VW8
VW9
VW10
Former tank
GREENHOUSE
HOUSE
0 10 20 30 40 50 FEET
0 5 10 15 METERS
EXPLANATION
• Nested vapor probes
U.S. Geological Survey ground-water observation well
New Jersey Department of Environmental Protection ground-water observation well
Multi-level ground-water sampler
Neutron probe access
Thermistor nest
Vapor extraction well
VW4 Vapor probe number

Figure 4. Site map and sampling locations at the research site, Galloway Township, New Jersey.

analyzer (TOC) was modified to measure the total amount of hydrocarbon in a vapor sample. Carbon dioxide concentrations also can be determined with this instrument.

Vapor is withdrawn from a probe by a peristaltic pump. The pump connects to the probe by a stainless-steel fitting which contains a septum access port. A vapor sample is collected by inserting a glass syringe through the septum and withdrawing a sample of the gas stream before it enters the pump tubing (fig. 7). These samples are then injected directly into analytical instruments.

Hydrocarbon vapors cause air in the unsaturated zone around residual gasoline to be denser than uncontaminated air. Diffusive transport of vapors away from the hydrocarbon source reduces air-phase density gradients. The magnitude of this density-driven advection in unsaturated zones contaminated with gasoline or other organic liquid contaminants such as chlorinated solvents is an area of active research. Bruell and others (1991, this Proceedings) conducted a series of column experiments covering a wide range of air-phase density gradients, including conditions that can occur with gasoline hydrocarbons.

SHALLOW GROUND-WATER QUALITY

Water-table depth significantly affects hydrocarbon transport from gasoline spills. Because gasoline is less dense than water, it tends to float on top of the water table in the capillary fringe. Tne floating gasoline provides a long-term source of hydrocarbons to underlying ground water. Furthermore, the water table acts as a barrier to the exchange of oxygen through the subsurface because effective diffusion constants in ground water can be as much as four orders of magnitude less than those in the unsaturated zone. Sharp gradients in hydrocarbon, electron-acceptor, and nutrient concentrations above and below the water table are measured at the Galloway site.

The ground-water-monitoring network at Galloway consists of submerged vapor probes, shallow observation wells, and multilevel samplers. Ground-water samples from this network are analyzed for selected hydrocarbons and organic acids which can form as intermediate microbial degradation products. Other indicators of hydrocarbon contamination and degradation also are determined: pH, and concentrations of alkalinity, dissolved oxygen, dissolved methane, ammonium, nitrate, nitrite, total Keldahl nitrogen, hydrogen sulfide, sulfate, total inorganic carbon, and dissolved organic carbon. Concentrations of ionic species,

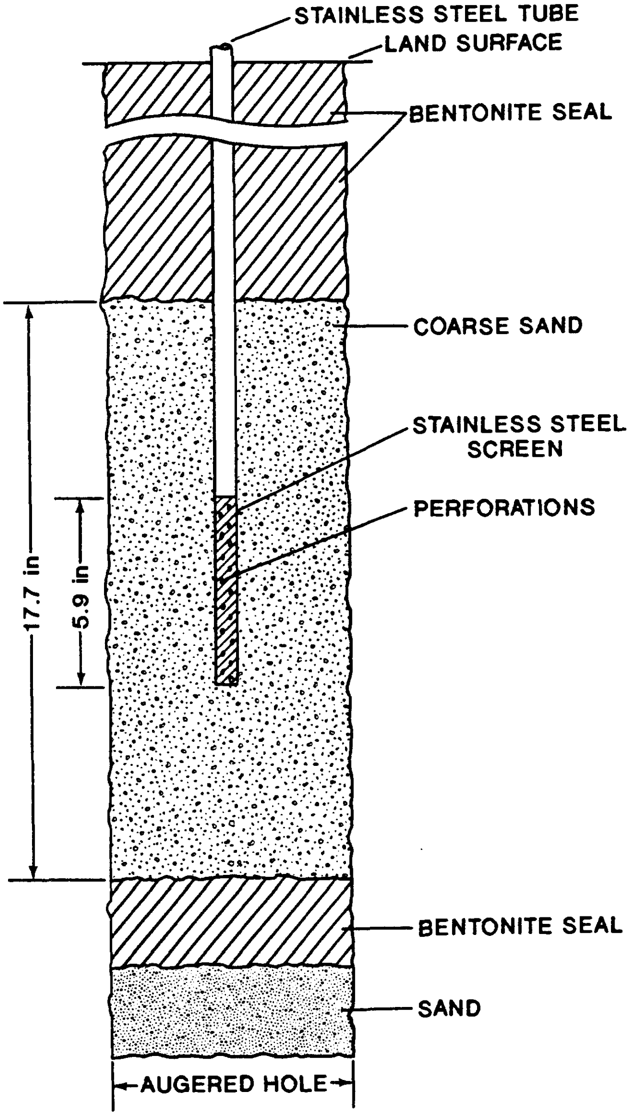

Figure 5. Schematic drawing of a vapor-probe nest installation.

such as iron, manganese, calcium, magnesium, sodium, potassium, silica, aluminum, strontium, and chloride, also are determined. These data and their application to hydrocarbon fate and transport research are discussed by Cozzarelli and others (1991, this Proceedings) and Baedecker and others (1991, this Proceedings).

SEDIMENT ANALYSIS FOR MICROBIAL ACTIVITY

The physical and chemical data base to be used to calibrate mathematical-transport models to estimate microbial degradation rates for hydrocarbons is complemented by analyses of sediment for microbial activity. In May 1990, sediment samples were collected from two locations one near vapor-probe nest 4 and the other near vapor-probe nest 9, to a depth of about 16 ft, by a manually driven, 1-in.-diameter, 2-ft-long split-spoon sampler. Mills and Randall (1991, this Proceedings) present microbial sediment analysis methods and preliminary results. The properties measured include total viable population counts and selected characteristics of hydrocarbon-specific degraders. Column experiments are being conducted to study the relation between unsaturated-zone gas transfer and the sediment microbial parameters cited above under controlled conditions (Baehr and others, 1991, this Proceedings). This research is designed to test hypotheses concerning the distribution of microbes in the subsurface independently. Subsamples of the split-spoon cores were collected to measure moisture content, bulk density, total porosity, and total hydrocarbon content. Total hydrocarbon content is determined by extracting the hydrocarbons from sediments with an organic solvent and analyzing the solvent-hydrocarbon mixture by using gas-chromatograph techniques. Additional cores will be collected after the initiation of venting remediation to determine the effects of venting on microbial populations. A shift toward aerobic bacteria is expected.

FIELD EXPERIMENTS AND PARAMETER ESTIMATION

Field experiments have been conducted at Galloway to determine the values of various parameters needed as input for mathematical models of hydrocarbon transport and microbial degradation. These field experiments include tracer, pneumatic, and air-sparging tests.

In June 1990, a tracer test was conducted by slowly diffusing fluorocarbons into the unsaturated zone near vapor-probe nest 9. From this experiment the air-phase diffusion coefficient in the unsaturated zone just above the perched water can be determined. The air-phase diffusion coefficient is needed to model the rate of exchange of unsaturated-zone gases. These results will assist in estimating *in situ* microbial hydrocarbon degradation. Air-phase diffusion coefficients were also determined in the laboratory for sediments collected during the installation of tracer-test instrumentation. These experiments are discussed further by Baehr and others (1991, this Proceedings).

Pneumatic tests of the unsaturated zone have been conducted to determine the air permeability of identified subsurface units. Pneumatic tests involve withdrawing air from individual vapor probes or vapor-extraction wells and recording the resulting air-pressure changes and flow rates in the unsaturated zone. Mini-pneumatic tests involve only one vapor probe and are designed to determine the air permeability of the sediment unit surrounding a vapor probe. These tests are discussed further by Welty and others (1991, this Proceedings). Larger-scale pneumatic tests also were conducted by pumping air through the vapor-extraction wells to quantify induced air movement through the unsaturated zone.

Air-sparging is an experimental remedial technique accomplished by injecting air beneath the water table. Air bubbles migrate upward and transfer hydrocarbon mass

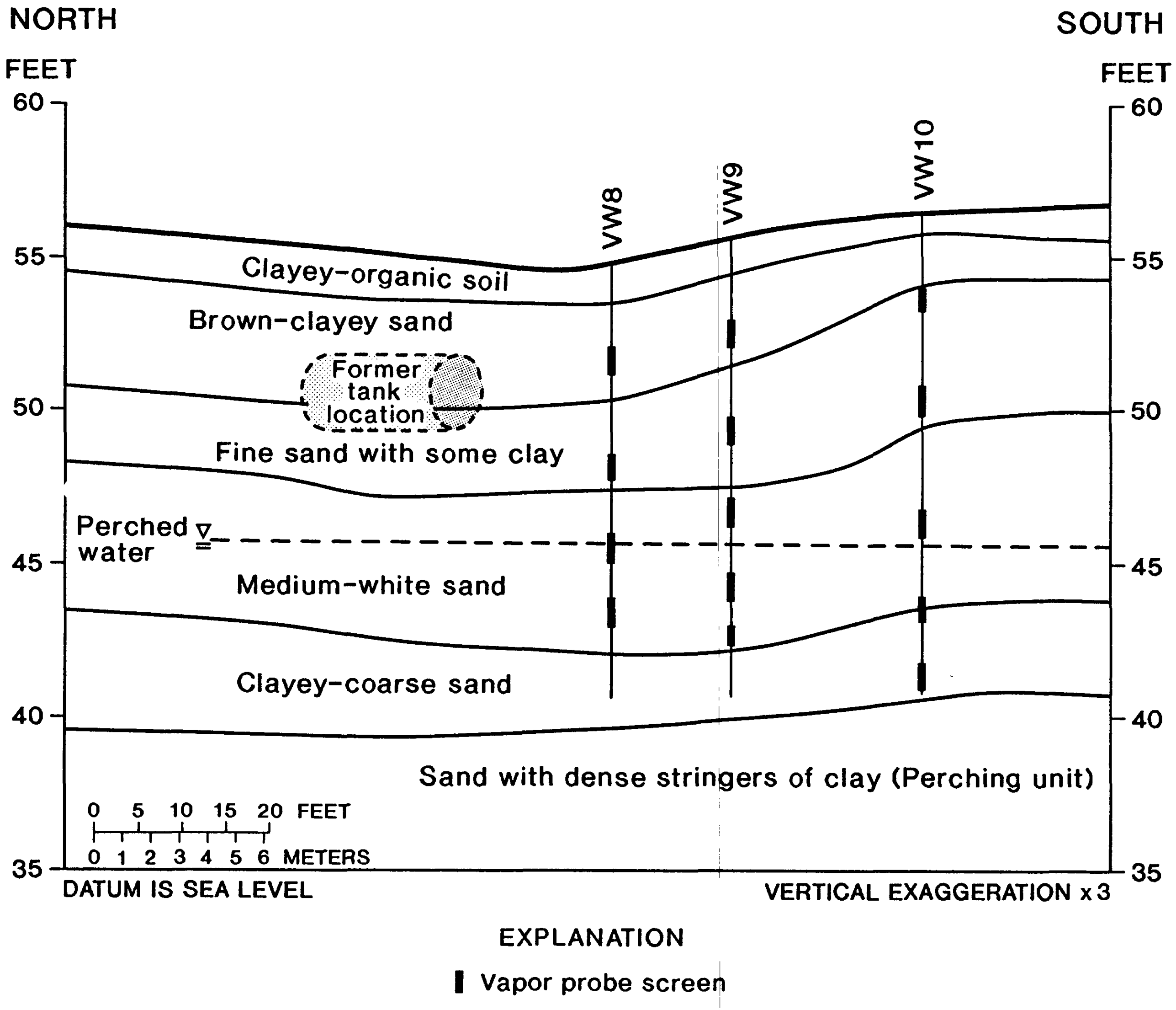
NORTH
SOUTH
FEET
FEET
60
55
50
45
40
35
VW8
VW9
VW10
Clayey-organic soil
Brown-clayey sand
Former tank location
Fine sand with some clay
Perched water
Medium-white sand
Clayey-coarse sand
Sand with dense stringers of clay (Perching unit)
0 5 10 15 20 FEET
0 1 2 3 4 5 6 METERS
DATUM IS SEA LEVEL
VERTICAL EXAGGERATION x3
EXPLANATION
▮ Vapor probe screen

Figure 6. Generalized hydrogeologic section through probe locations 8, 9, and 10 illustrating relation among submerged probes, perched water, and site geology.

across the water table into the unsaturated zone where the hydrocarbons can be removed either by induced venting or by aerobic microbial degradation. Oxygen also is recharged to contaminated ground water. In August 1990, two pilot-scale air-sparging tests were conducted. The purpose of these pilot tests was to determine the rate of mass transfer across the water table caused by an air-bubble stream and to study the dissipation of hydrocarbons in the unsaturated zone caused by diffusion and degradation after air injection ceased.

SUMMARY

This paper presents a description of the investigations comprising a subsurface hydrocarbon-transport research project at a gasoline spill site in Galloway Township, N.J. To date (December 1990), project accomplishments have centered on site instrumentation, methods development, data acquisition, and preliminary model development. The contributions of 16 investigators are summarized and highlight the interdisciplinary effort to achieve project objectives.

Data collected at the Galloway Township site include the composition of unsaturated-zone vapors and shallow ground-water quality from an areally and vertically intensive monitoring network. Field experiments have been conducted to estimate parameters for mathematical modeling of hydrocarbon fate in the subsurface. The physical and chemical data base to be used to calibrate the mathematical transport models is complemented by sediment analysis for microbial activity. Laboratory experiments are being conducted to rigorously test submodel hypotheses.

Future plans include site remediation, using induced venting in conjunction with ground-water air sparging. The data-collection program will continue during the remedial phase because of the unique opportunity afforded by the

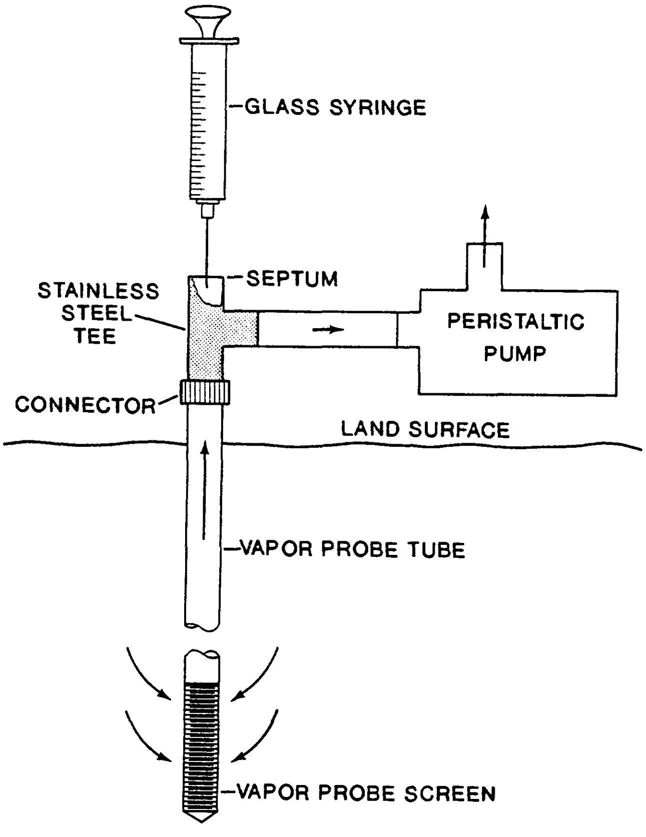

Figure 7. Method for extracting a vapor sample from a probe.

changing geochemical conditions expected. Field and laboratory results will be incorporated into the development and application of mathematical models of the transport and fate of hydrocarbons in the subsurface, which will provide transfer value to other sites contaminated by hydrocarbons.

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METHOD FOR ESTIMATING RATES OF MICROBIAL DEGRADATION OF HYDROCARBONS BASED ON GAS TRANSPORT IN THE UNSATURATED ZONE AT A GASOLINE-SPILL SITE IN GALLOWAY TOWNSHIP, NEW JERSEY

By Arthur L. Baehr[1], Jeffrey M. Fischer[1], Matthew A. Lahvis[1], Ronald J. Baker[1], and Nicholas P. Smith[1]

ABSTRACT

An approach is presented for estimating rates of microbial degradation of hydrocarbons at a gasoline-spill site. The method is based on modeling oxygen and carbon dioxide transport in the unsaturated zone. The distribution of these gases in the unsaturated zone at the Galloway Research Site, New Jersey, provides a distinctive sitewide indication of hydrocarbon degradation. Calibration of a mathematical transport model with these data will allow for computation of hydrocarbon degradation rate. Field and laboratory experiments were conducted to determine the soil diffusion coefficient, a parameter required by the transport model. The field experiment was conducted by slowly injecting fluorocarbon tracers into the unsaturated zone and monitoring the resulting diffusive transport. Laboratory experiments were conducted in columns packed with sediment from the Galloway site.

INTRODUCTION

Microbial degradation of hydrocarbons in the subsurface is a significant phenomenon associated with petroleum product spills. Hazardous hydrocarbon constituents of petroleum products, such as benzene, toluene, and xylene, can contaminate ground-water resources. These and other compounds can be microbially degraded in the unsaturated zone and shallow ground water. Thus microbial degradation, combined with volatile loss of hydrocarbons at land surface, can provide natural cleansing of product spills. Quantification of these natural cleansing mechanisms can be of relevance to regulators faced with the decision to enforce site remediation or to evaluate the consequence of partial remediation.

Hydrocarbon degradation by microbes can be determined in vitro by means of microcosm experiments with sediments collected from the site. *In-situ* degradation rates can be inferred from such experiments by making extrapolating assumptions pertaining to microbial growth rates and nutrient availability. This type of analysis of sediments collected from the Galloway gasoline-spill site is discussed by Mills and Randall (1991, this Proceedings). Microcosm experiments are extremely labor-intensive, however. Therefore, estimation of hydrocarbon-degradation rates by microcosm experiments is impractical, and the estimation of seasonal variations in degradation rates by such experiments is infeasible. Although standard microbiological techniques are required for microbe identification and determination of specific degradation pathways, another, more practical technique is needed to calculate site-specific microbial degradation rates as a function of time and space.

This paper presents an alternative approach for estimating rates of microbial degradation of hydrocarbons at a gasoline-spill site. Site hydrogeology is discussed by Fischer and others (1991, this Proceedings). The approach is based on the simulation of oxygen and carbon dioxide transport in the unsaturated zone. The distribution of these unsaturated-zone gases at the Galloway gasoline-spill site provides a distinctive sitewide indication of hydrocarbon degradation. In addition, field and laboratory experiments designed to determine the soil diffusion coefficient are presented.

Figure 1 illustrates the distribution of oxygen as a percentage of unsaturated-zone gas along a vertical section at the Galloway Township site in December 1989. Construction of vapor probes (indicated by boxes in fig. 1) and gas sampling methods used in this approach are discussed by Fischer and others (1991, this Proceedings). Gas chromatography was used to determine the composition of unsaturated-zone vapors (Baker and others, 1991, this Proceedings). Dissolved-oxygen concentration was determined for water samples collected from probes submerged in perched water along this section using the Winkler method. The water sampled was virtually anoxic along the cross section. The oxygen distribution suggests the presence of an active aerobic microbial community near the perched water table. Furthermore, because dissolved gasoline hydrocarbons are present at high concentrations in the perched water but are not found in the unsaturated zone (which contains oxygen) above the perched water, we assume that the rate of oxygen diffusion into the perched water is the rate-limiting step for aerobic hydrocarbon degradation. The end products of complete aerobic hydrocarbon degradation are carbon dioxide and water. Therefore, the production of carbon dioxide and its distribution in unsaturated-zone gas are related to oxygen consumption during biodegradation. Figure 2 illustrates the distribution of carbon dioxide, as a percentage of unsaturated-zone gas, determined from the same samples used to produce the oxygen profile illustrated in figure 1.

Carbon dioxide also is an end product of anaerobic degradation. Therefore, the amount of carbon dioxide in the unsaturated zone could exceed that accounted for by the oxygen deficit caused by aerobic microbes. Carbon dioxide concentrations were determined for water samples collected from submerged probes by determining alkalinity and pH and assuming that the carbonate system was in equilibrium. This determination of the perched-water boundary condition with respect to carbon dioxide in addition to unsaturated-zone gas determination should allow for a separation of carbon dioxide produced by aerobic and anaerobic communities.

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APPROACH

A mathematical model of the transport of unsaturated-zone gases is required to calculate rates of oxygen and carbon dioxide movement implied by the oxygen and carbon dioxide contours illustrated in figures 1 and 2. Air-phase diffusion will be assumed to dominate water-phase diffusion and advective contributions to flux caused by water infiltration and atmospheric-pressure variations (Baehr, 1987). Therefore, vapor diffusion is the only transport mechanism simulated. Furthermore, as a first approximation, quasi-steady-state gas distribution in the unsaturated zone will be assumed. This assumption implies that the time scale during which the characteristics of the microbial communities change (responding to, for example, changes in temperature and dissolved hydrocarbon concentrations) is large compared to the time scale during which gases physically redistribute in the unsaturated zone. The model then is a short-term simulation with microbial community changes held constant. With these assumptions, the transport of air-phase constituents and the microbial degradation of hydrocarbons is simulated by using a series of steady-state equations, as follows (Baehr, 1987):

$$\nabla \bullet [D_k\theta \ \tau \ \nabla \ G_k] = R_k \qquad (1)$$
$$k = 1, 2, ..., N,$$

where

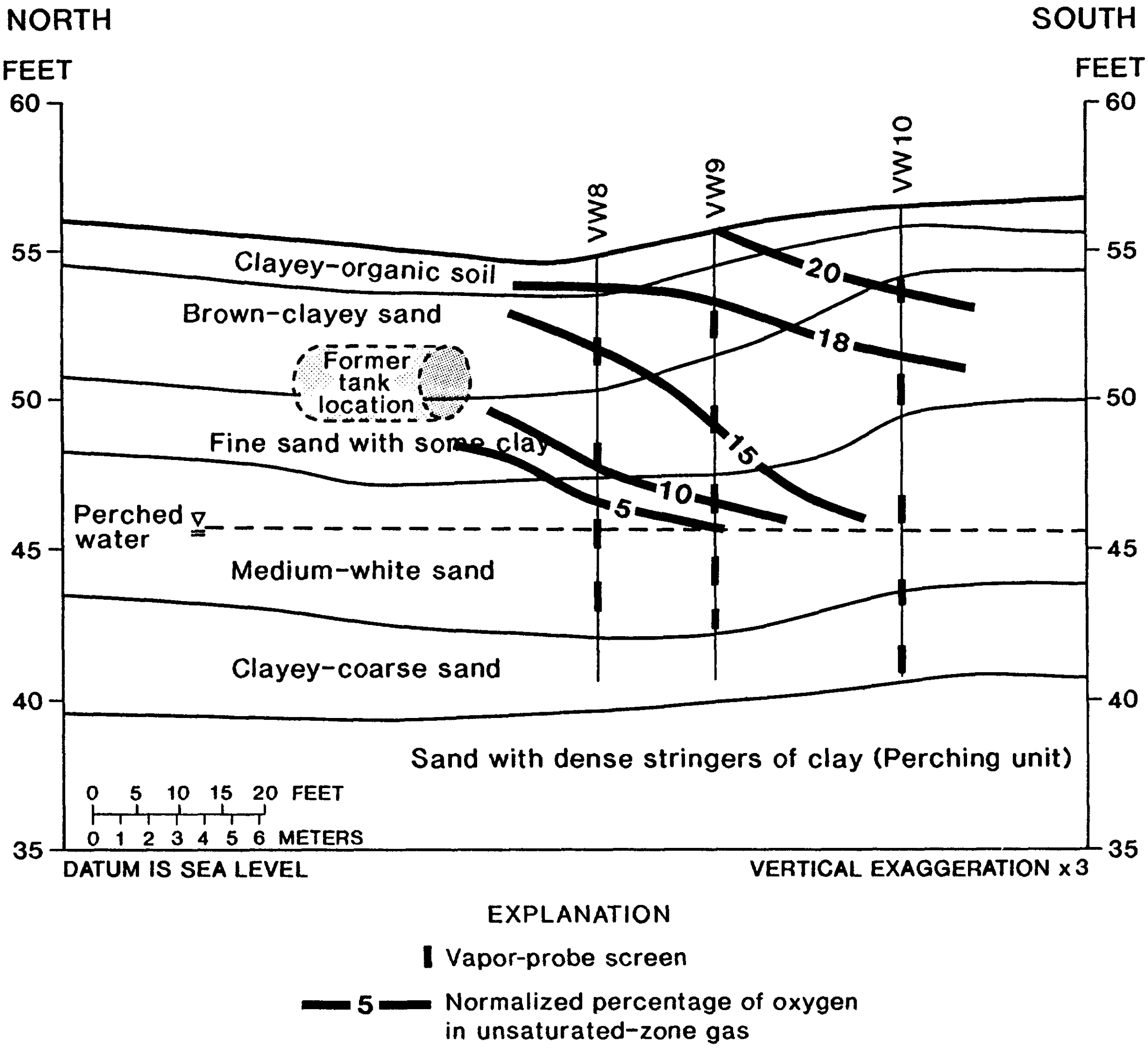
D_k is the bulk air diffusion coefficient for the k^{th} constituent of the unsaturated zone air phase (in centimeters, squared per second),

θ is air-filled porosity (unitless), τ is tortuosity (unitless),

G_k is the concentration of the k^{th} constituent in the air phase (in grams per centimeters, cubed),

R_k is the source or sink term resulting from microbial reactions (in grams per centimeters, cubed per second), and

N is the total number of air-phase constituents.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Clayey-organic soil
Brown-clayey sand
Former tank location
Fine sand with some clay
Perched water
Medium-white sand
Clayey-coarse sand
Sand with dense stringers of clay (Perching unit)
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DATUM IS SEA LEVEL
VERTICAL EXAGGERATION x3
EXPLANATION
Vapor-probe screen
5 Normalized percentage of oxygen in unsaturated-zone gas

Figure 1. Vertical section showing distribution of oxygen as a percentage of unsaturated zone gas at the Galloway Township, New Jersey, gasoline-spill site, December 1989.

The soil parameters θ and τ vary in space as a function of heterogeneity in site lithology. Coupling of constituent transport can occur by the terms R_k. A three-dimensional version of equation (2) will be utilized.

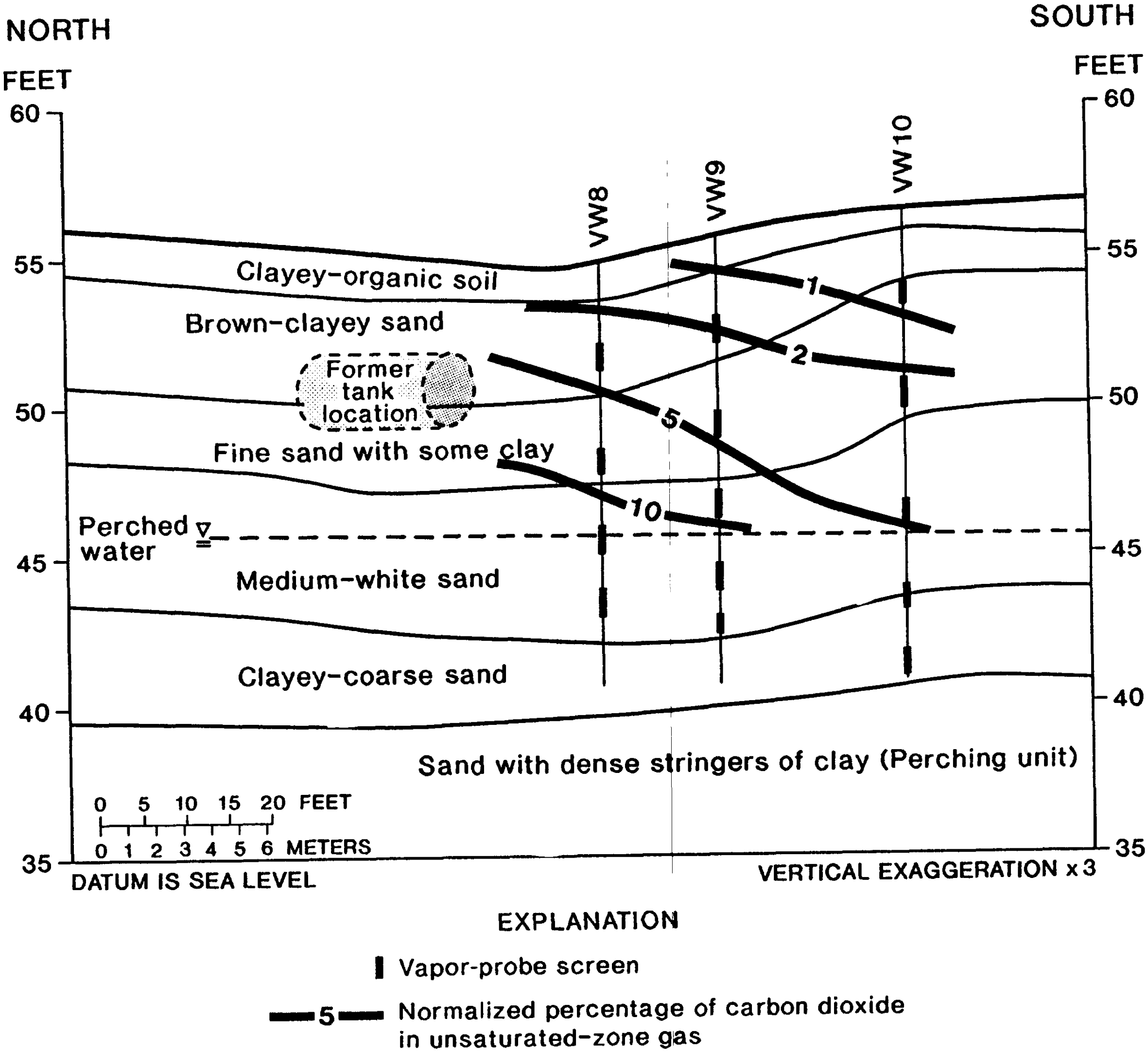
The distribution of gases (G_k) is determined by measurements in the unsaturated zone. Bulk air diffusion coefficients (D_k) can be calculated for each constituent (Fuller and others, 1966). Air-phase porosity (θ) can be determined by sediment analysis and neutron logging, and tortuosity (τ) can be estimated or determined by field or laboratory tracer tests as discussed in the following section. The distributed microbial degradation rates (R_k) are unknown and will be determined by model calibration for each constituent. Integration of these rates over the site will provide the alternative method to approximate sitewide microbial degradation. For example integration of the calibrated oxygen depletion rate over the domain will provide a sitewide estimate for the aerobic degradation rate of hydrocarbons assuming an averaged stoichiometric relation between total hydrocarbon degradation and oxygen consumption.

DATA COLLECTION

The data-collection program described below is being conducted at the Galloway Township site to provide data for the calculation of hydrocarbon degradation rates proposed in the previous section.

Unsaturated Zone Vapor Measurements and Evaluation of the Water-Table Boundary Condition

Figures 3 and 4 illustrate the areal distribution of oxygen and carbon dioxide, respectively, as a percentage of unsaturated zone gas at a depth of about 6 ft (feet) below land surface. Similar contour maps could be constructed at other probe elevations (see figs. 1 and 2). The figures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Clayey-organic soil
Brown-clayey sand
Former tank location
Fine sand with some clay
Perched water
Medium-white sand
Clayey-coarse sand
Sand with dense stringers of clay (Perching unit)
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DATUM IS SEA LEVEL
VERTICAL EXAGGERATION x3
EXPLANATION
Vapor-probe screen
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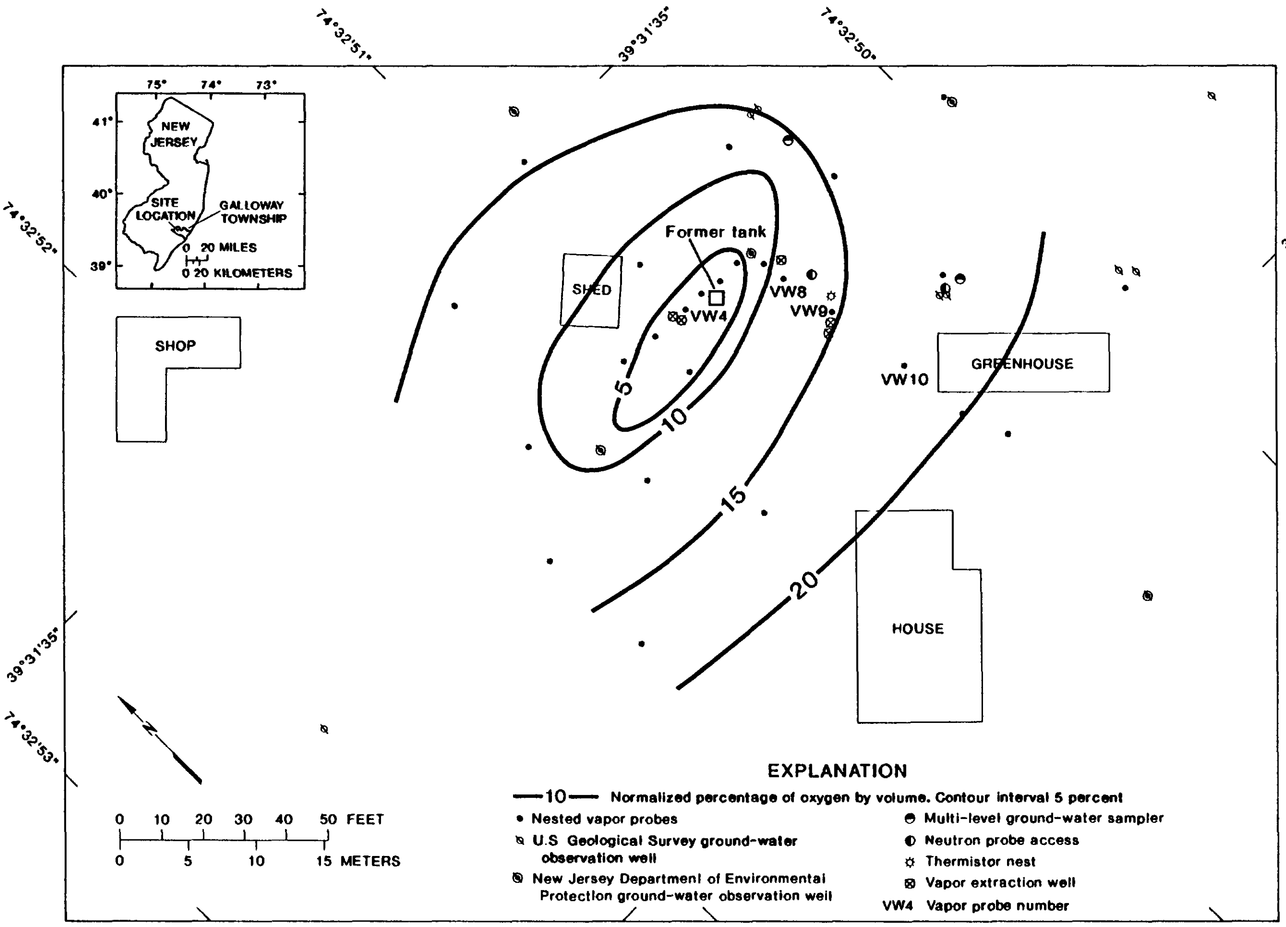
Normalized percentage of carbon dioxide in unsaturated-zone gas

Figure 2. Vertical section showing distribution of carbon dioxide as a percentage of unsaturated zone at the Galloway Township, New Jersey, gasoline-spill site, December 1989.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NEW JERSEY
SITE LOCATION
GALLOWAY TOWNSHIP
0 20 MILES
0 20 KILOMETERS
SHOP
SHED
Former tank
VW4
VW8
VW9
VW10
GREENHOUSE
HOUSE
5
10
15
20
N
0 10 20 30 40 50 FEET
0 5 10 15 METERS
EXPLANATION
—10— Normalized percentage of oxygen by volume. Contour interval 5 percent
Nested vapor probes
U.S Geological Survey ground-water observation well
New Jersey Department of Environmental Protection ground-water observation well
Multi-level ground-water sampler
Neutron probe access
Thermistor nest
Vapor extraction well
VW4 Vapor probe number

Figure 3. Areal distribution of oxygen as a percentage of unsaturated zone gas at a depth of 6 feet below land surface at the Galloway Township, New Jersey, gasoline-spill site, December 1989.

illustrate sitewide distribution of oxygen and carbon dioxide as a result of hydrocarbon microbial degradation. Measurements of oxygen and carbon dioxide in the unsaturated zone were conducted on the following dates to document seasonal and temporal variations: July 1989, December 1989, April 1990, June 1990, and August 1990.

In order to determine the boundary condition represented by the perched water table, water samples collected from submerged probes with a peristaltic pump are analyzed for dissolved oxygen, alkalinity, pH, selected hydrocarbons, organic acids, and other constituents (Baedecker and others, 1991, this Proceedings). The corresponding vapor-phase boundary condition at the water table will be determined from the water-quality data by assuming partitioning according to Henry's Law.

Temperature and Moisture Profiles andSediment Analysis

A nest of thermistors located near vapor probe nest 9 allows for recording temperature over 1-ft intervals at depths from 1 to 23 ft. Figure 5 shows plots of temperature as a function of depth below land surface for a profile (March 27, 1989) of cool conditions and a profile (September 25, 1989) of warm conditions. At a depth of 10 ft, which corresponds approximately to the location of the microbially active perched water table, a seasonal variation of about 10° C (degrees Celsius) is observed. Because bulk air diffusion coefficients and the model for microbial degradation are functions of subsurface temperature, it is anticipated that seasonal variations in microbial degradation of hydrocarbons will occur.

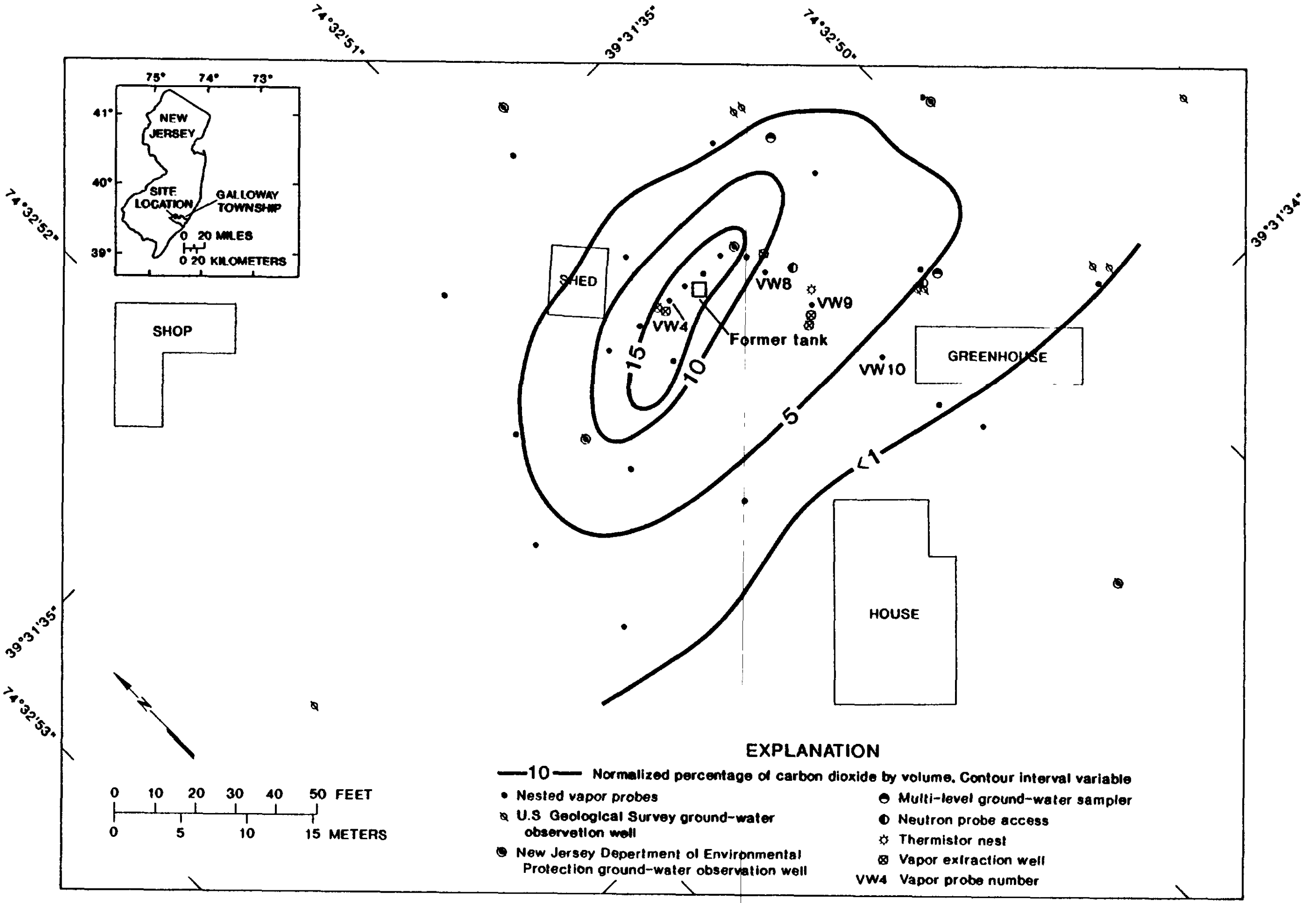
Effective air-phase diffusion coefficients, ($D_k\theta_T$) depend greatly on soil-moisture content. Tortuosity can be approximated as a function of moisture content by using the following relation of Millington and Quirk (1961):

$$\tau = \frac{\theta^{7/3}}{\theta_T^2}, \qquad (2)$$

where

θ is air filled porosity, and
θ_T is total porosity.

Temporal variation in the unsaturated zone moisture profile is monitored at two locations with a neutron probe. Total porosity has been determined at many locations including the two locations where the neutron probe access tubes were installed. Data are used to calculate effective diffusion coefficients in equation 1 using the estimate of tortuosity given by equation 2.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NEW JERSEY
SITE LOCATION
GALLOWAY TOWNSHIP
0 20 MILES
0 20 KILOMETERS
SHOP
SHED
VW8
VW9
VW4
Former tank
VW10
GREENHOUSE
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0 5 10 15 METERS
EXPLANATION
—10— Normalized percentage of carbon dioxide by volume. Contour interval variable
• Nested vapor probes
U.S Geological Survey ground-water observation well
New Jersey Department of Environmental Protection ground-water observation well
Multi-level ground-water sampler
Neutron probe access
Thermistor nest
Vapor extraction well
VW4 Vapor probe number

Figure 4. Areal distribution of carbon dioxide as a percentage of unsaturated zone gas at a depth of 6 feet below land surface at the Galloway Township, New Jersey, gasoline-spill site, December 1989.

The unsaturated zone consists of at least four lithologic units as illustrated in figure 1. Site lithology was extensively mapped during the installation of the vapor-probe network by describing cuttings from hand- augered holes. Because these units have different diffusive properties, the model allows for spatial variations in tortuosity and air-filled porosity; otherwise, changes in gradients of oxygen and carbon dioxide may be falsely interpreted as changes in the source/sink terms.

Use of Tracer Tests to Determine Diffusion Coefficients

Evaluation of the effective diffusion coefficient ($D_k\theta\tau$) requires an estimate of tortuosity, τ. A field determination of this parameter supplements the Millington-Quirk estimate based on sediment analysis given by equation 4. A tracer test was conducted in June 1990 to evaluate this parameter *in situ*. Two fluorocarbons, F-11 and F-23, were injected slowly through a vapor probe at a depth of 7.4 ft that was installed approximately 1.6 ft from the nest 9 vapor probes located at depths of 3, 6, and 8.2 ft. The probes were sampled over a period of 3 days to record the breakthrough

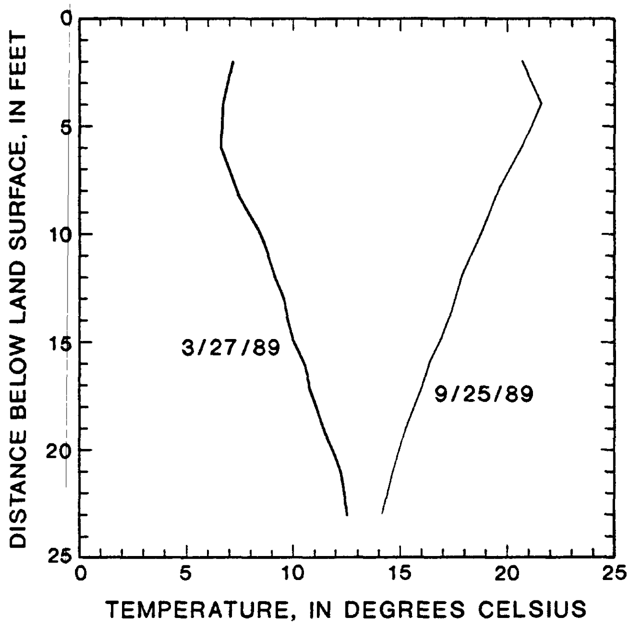

Figure 5. Subsurface temperature profiles at the Galloway Township, New Jersey, gasoline-spill site.

of the tracers. The same probes were sampled for a period of 2 weeks after tracer injection ceased. Fluorocarbon concentrations were determined by using gas chromatography and a flame ionization detector. A mathematical model of vapor diffusion will be calibrated to determine tortuosity from this field test. This tracer test is similar to the one conducted by Kraemer and others (1988).

Laboratory Column Experiments

Unsaturated soil-column experiments are being conducted to determine effective diffusion coefficients independently. Sediments collected during installation of the tracer-test injection well were packed into a column. The flux of xylene was measured through the column, and tortuosity of the lithologic unit above perched water was determined by calibrating a one-dimensional diffusion model. The design of this type of experiment is discussed by Bruell and others (1991, this Proceedings).

Column experiments are currently being conducted to determine microbial degradation rates under controlled conditions. Sieved fractions of Galloway sand are packed in glass columns and suspended from a reservoir containing the hydrocarbon source, which diffuses upward through the column. Soil gas is periodically analyzed to determine the change in composition due to microbial activity. For example, under aerobic conditions carbon dioxide production is measured to determine a degradation rate. After degradation stabilizes, the column is disassembled and microbial populations are characterized at various depths. Information gained from these column experiments should be useful in calibrating the field-scale model.

SUMMARY

Microbial degradation is an important natural cleansing mechanism for hydrocarbons in the subsurface at gasoline-spill sites. Techniques for determining rates of microbial metabolism based on extrapolation of results of microcosm experiments are impractical for determining degradation rates throughout a site as well as for documenting the seasonal variability of these rates. Therefore, a method was developed for calculating sitewide and seasonally variable microbial-degradation rates of hydrocarbons on the basis of the transport of gases in the unsaturated zone.

An active hydrocarbon-degrading microbial community exists in perched water at the Galloway Township site. The diffusion rate of oxygen in the unsaturated zone limits the activity of the aerobic community. Upward diffusion of carbon dioxide in the unsaturated zone from perched water provides an indication of both aerobic and anaerobic degradation. Field and laboratory experiments were conducted to estimate unsaturated zone diffusion coefficients, which are required by vapor transport models. A transport model of gas diffusion will be calibrated to obtain degradation rates.

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GEOCHEMICAL GRADIENTS IN SHALLOW GROUND WATER CAUSED BY THE MICROBIAL DEGRADATION OF HYDROCARBONS AT GALLOWAY TOWNSHIP, NEW JERSEY

By Isabelle M. Cozzarelli[1], Mary Jo Baedecker[1], and Jessica A. Hopple[1]

ABSTRACT

A study of the geochemical gradients and alterations in ground water adjacent to a gasoline spill in Galloway Township, New Jersey, was undertaken to examine the geochemical effects of the microbial degradation of organic contaminants in part of the New Jersey Coastal Plain. A detailed study of the ground-water geochemistry in a vertical section of the aquifer indicates that ground water near the gasoline source was severely affected by the hydrocarbon contaminants and that the vertical changes of geochemical constituents were significant. The concentration of dissolved hydrocarbons, mostly aromatic hydrocarbons, reached a maximum of 33.6 milligrams per liter in anoxic ground water at 15.5 feet below land surface. The highest concentrations of organic acids (1.6 milligrams per liter) are found in this same location (15.5 feet below land surface) where aromatic hydrocarbons were at high concentrations throughout the study period (June 1989 through July 1990). The reactions controlling the distribution of hydrocarbons and organic acids are microbially mediated oxidation-reduction reactions. The important degradation reactions in the shallow ground water are nitrate reduction, iron reduction and sulfate reduction. Below a depth of 18 feet, aerobic degradation and, to a lesser extent, nitrate reduction occur. These reactions cause significant geochemical alterations of the ground-water chemistry and aquifer solids.

INTRODUCTION

Gasoline is a mixture of hydrocarbons that have a wide range of physical characteristics and considerable diversity in their geochemical fate in the environment. The aqueous solubilities of the different types of hydrocarbons differ significantly. When gasoline comes in contact with ground water, the more soluble components are preferentially leached into the water. Benzene, with a solubility in pure water of 1,780 mg/L (milligrams per liter) is one of the most soluble hydrocarbons in gasoline. In addition, mononuclear aromatic hydrocarbons do not significantly sorb onto aquifer solids with low organic content, and, therefore, they can be rapidly transported (Schwarzenbach and Westall, 1981).

Hydrocarbons are unstable in ground water. Thermodynamics dictate that unstable compounds will undergo reactions when they are out of equilibrium with their present environment. These reactions consist largely of microbially mediated oxidation-reduction reactions. The ultimate fate of the hydrocarbons is thus, in large part, a function of their biodegradability in the geochemical environment. Laboratory studies have shown that benzene, toluene, and xylenes can be degraded under aerobic, denitrifying (Kuhn and others, 1988; Major and others, 1988), iron reducing (Lovley and others, 1989) and methanogenic (Wilson and others, 1986; Grbić-Galić and Vogel, 1987) conditions. As a result of these processes, new compounds, such as low-molecular weight organic acids, are formed that were not present initially in the source material. Metabolism of aromatic acids such as benzoic acid under anaerobic conditions is well known (Tarvin and Buswell, 1934; Nottingham and Hungate, 1969; Evans, 1977; Ferry and Wolfe, 1977; Mountfort and Bryant, 1982). The microbial degradation of hydrocarbons and organic acids can result in changes in the oxidation-reduction potential and overall geochemistry of ground water and alterations in the mineral composition of aquifers.

A surficial aquifer contaminated with leaded gasoline is currently being examined for the effects of organic contaminant degradation on the ground-water chemistry of a local part of the New Jersey Coastal Plain. This paper presents the results of an intensive study of the geochemical gradients and alterations in ground water at a location close to the gasoline spill. This particular site was chosen for detailed study because the ground water appeared to be severely affected by hydrocarbon contaminants and because the vertical changes of geochemical constituents were significant. The results of this work will provide additional insight into the geochemical reactions that control the fate of aromatic hydrocarbons and into the geochemical alterations caused by the presence of the hydrocarbons and organic-acid intermediates in the subsurface.

FIELD SITE

The field site is located in Galloway Township, N.J., 10 miles west of Atlantic City. An underground storage tank on a farmer's property leaked, resulting in the accumulation of a separate gasoline phase in the saturated and unsaturated zones of this shallow aquifer (Fischer and others, 1991, this Proceedings). The aquifer is in surficial sediments of the Bridgeton Formation, described as fluvial feldspathic deposits (Owens and Minard, 1979). The upper 20 ft (feet) of soil at the site is predominately fine to medium sand with iron-oxide coatings and discontinuous clay lenses and coarse-sand lenses throughout. Below a depth of 20 ft, coarse sand predominates. At approximately 11 to 15 ft below land surface, a clayey-sand layer contains 1- to 3-in. (inch) -thick, dense, clay lenses that have a low hydraulic conductivity. 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 aquifer was approximately 14 to 17 ft below land surface during the study period (June 1989 to July 1990). The hydraulic gradient of the water table aquifer is small (0.004).

METHODS

Water samples were collected six times over a 1-year period from June 1989 to July 1990. In this study, ground-water samples were collected from stainless-steel

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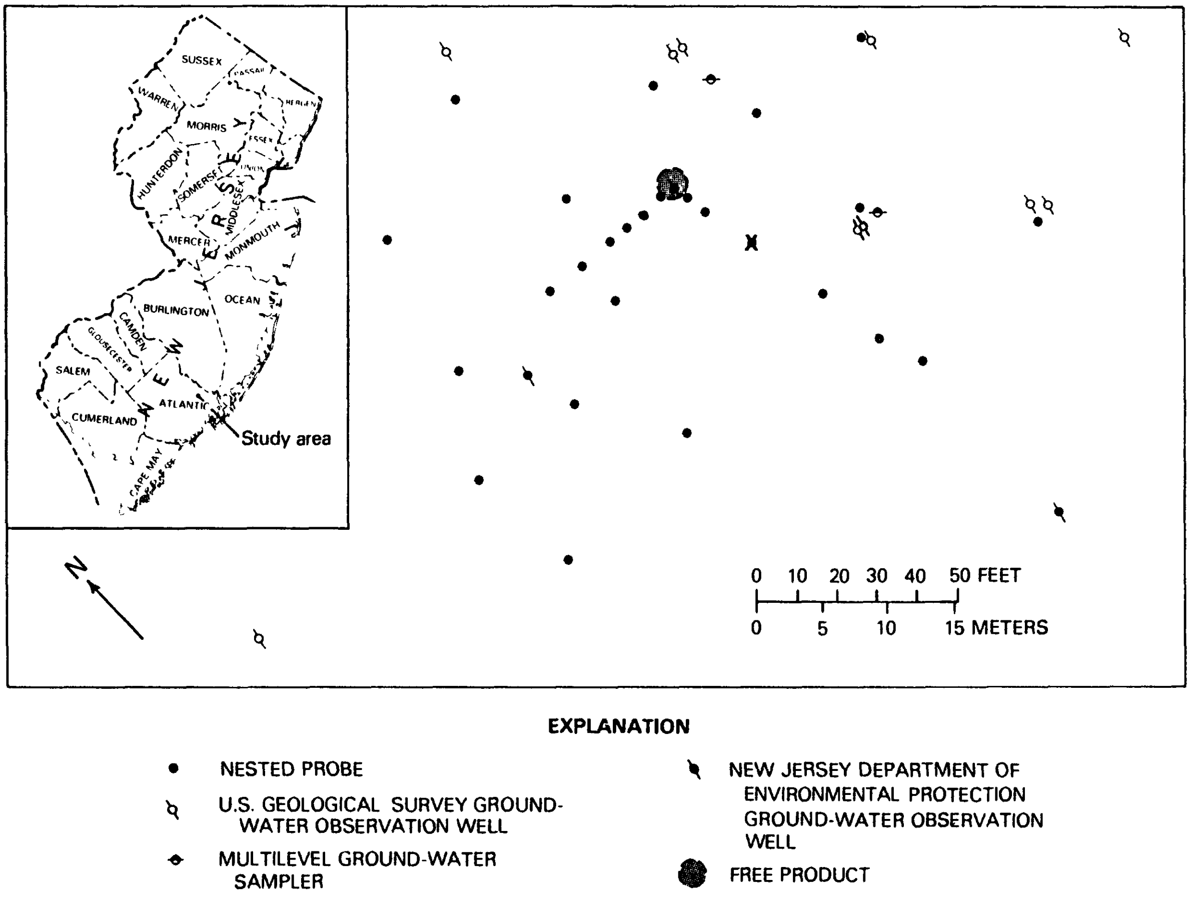
[1] U.S. Geological Survey, Reston, Va.

probes installed in the perched water and below the water table (fig. 1, nested probe). The probes consist of stainless-steel tubing (1/4 in.) perforated over a 6 in. interval and set at the desired sampling depths (Fischer and others, 1991, this Proceedings). Several probes at various depths (approximately 2-3 ft apart) were installed at one location. This paper focuses on a vertical series of probes located 25 ft south of the location of free product (gasoline) in the subsurface (fig. 1). Probes at this location were installed at 10.7, 12.5, 15.5, 18, and 22 ft below land surface, tapping both the perched and regional water zones. The areal distribution of hydrocarbon contaminants and unstable constituents are described in Baedecker and others (1991, this Proceedings).

Water samples were collected from the probes with a peristaltic pump (Baedecker and others, 1991, this Proceedings). Water samples were analyzed for geochemical constituents that are important reactants, intermediates, or end products involved in the degradation of the dissolved hydrocarbons. Major cations and anions were also analyzed to obtain complete geochemical characterization of the ground water. Temperature, pH, specific conductance, and alkalinity (reported as bicarbonate) were measured in the field. Syringes were used to collect hydrogen sulfide and methane to eliminate exposure of the samples to oxygen. Redox-sensitive constituents, including dissolved organic carbon, bicarbonate, oxygen, ammonia, hydrogen sulfide, ferrous iron, and methane, were analyzed as described in Baedecker and Cozzarelli (1991). Nitrate, sulfate, and chloride were analyzed on filtered (0.4 µm (micrometer)) samples by ion-exchange chromatography on a Dionex series 4000i[2]. Concentrations of calcium, magnesium, sodium, potassium, silica, manganese, strontium, total iron and aluminum, were measured on filtered (0.2 µm) and acidified (0.5 percent HCl) samples by direct-current plasma emission spectrometry on an ARL SpectroSpan V[2].

Samples were collected for $\delta^{13}C$ of total inorganic carbon by precipitating the carbon as strontium carbonate ($SrCO_3$) in the field from 0.4 µm-filtered samples (Gleason and others, 1969). The precipitate was removed from the solution by filtration in the laboratory, rinsed with deionized water, dried, and acidified with phosphoric acid. The carbon dioxide (CO_2) evolved was purified and analyzed on a Dupont[2] isotope-ratio mass spectrometer.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N
X
0 10 20 30 40 50 FEET
0 5 10 15 METERS
EXPLANATION
NESTED PROBE
U.S. GEOLOGICAL SURVEY GROUND-WATER OBSERVATION WELL
MULTILEVEL GROUND-WATER SAMPLER
NEW JERSEY DEPARTMENT OF ENVIRONMENTAL PROTECTION GROUND-WATER OBSERVATION WELL
FREE PRODUCT

Figure 1. Map of the study area showing location of the subsurface gasoline phase and ground water sampling sites. X marks the location of the nest of vertical sampling probles that were sampled throughout the study period.

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[2] Use of brand or trade names in this paper is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

Water samples for hydrocarbon analyses were collected in brown glass bottles, preserved with mercuric chloride, and amended with a spiking solution containing deuterated orthoxylene. The hydrocarbons were extracted from the water and concentrated using a liquid-liquid extraction technique described in Baedecker and others, 1991, this Proceedings). Samples for analysis of organic acids were preserved with mercuric chloride and 1 normal potassium hydroxide to minimize losses from degradation and volatilization that may be significant for low-molecular weight acids at pH less than 10 (Sansone and Martens, 1981). Samples were freeze-dried and then acidified with phosphoric acid. Organic acids were extracted from the acidic solution with diethyl ether and quantified by gas chromatography with flame-ionization detection. Positive identification of acid structures was made on selected samples by coinjection of samples and authentic standards and by gas chromatography/mass spectrometry.

RESULTS

Ground water in the vicinity of the gasoline source is highly contaminated with hydrocarbons. In the shallow ground water, the most abundant hydrocarbons are benzene, toluene, ethylbenzene, xylenes, and 1,2,4 trimethyl benzene. Aliphatic hydrocarbons were not found in the ground water. The concentrations of total aromatic hydrocarbons (mono and dicyclic aromatic hydrocarbons with 0-4 substituent alkyl carbons) are shown in figure 2. These data were obtained from the discrete-interval sampling probes in June 1989, and January, February, April, May, and July 1990, respectively, at location X in figure 1. The concentrations of hydrocarbons in June 1989 were less than at any time in 1990. Hydrocarbon concentrations reached a maximum of 33.6 mg/L in ground water just above the clay lens 15.5 ft below land surface in July 1990 (fig. 2).

The organic-acid pool contains aliphatic as well as aromatic carboxylic acids. The organic acids identified in the ground water at location X (fig. 1) are shown in table 1. The most abundant aliphatic acid is acetic acid. The aromatic acids are mostly methyl and dimethyl benzoic acid as well as phenyl acetic-acid structures. The highest concentrations of acids are in the anoxic shallow ground water (1.6 mg/L total identifiable organic acids 15.5 ft below land surface) where aromatic hydrocarbons were at high concentrations throughout the study period (fig. 2). The predominant organic acid found was a dimethyl benzoic acid (the 2,4 and(or) 2,5 isomer).

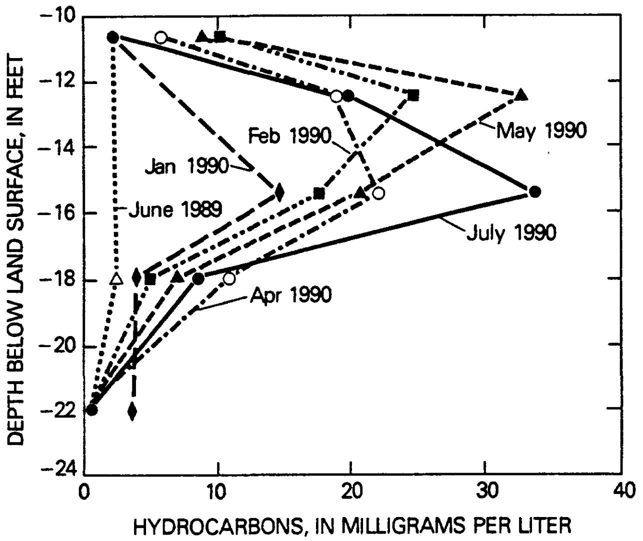

Figure 2. Concentrations of total hydrocarbons, in milligrams per liter, as a function of depth below land surface at location X between June 1989 and July 1990.

The distributions of dissolved oxygen, nitrate, and sulfate with depth in the aquifer were analyzed for three time periods (fig. 3 a, b, and c). Concentrations of these constituents differ significantly over small vertical distances. The shallow, perched ground water was anoxic throughout the study period. There was a small amount of oxygen present at depths of 18 to 22 ft in the water table aquifer. Nitrate was absent in the shallower probes and sulfate was at low levels (<0.12 mM (millimolar)). Analysis of reduced chemical species (fig. 4) revealed that the concentrations of ammonia, ferrous iron, and hydrogen sulfide were higher above the clay than below the clay. Methane was detected at low concentrations (<0.01 mM). The distributions of oxidized and reduced species show changes with time over the period of study. The most significant changes occurred between June 1989 and February 1990 when O_2, NO_3, and SO_4 decreased and NH_4, Fe, and H_2S increased.

Table 1. *Concentrations of organic acids identified in shallow ground water near the gasoline source (location X, fig. 1)*

(µg/L, micrograms per liter; <, less than)

Organic acid	Concentration (µg/L)
Acetic	147
Propanoic	<2
Benzoic	3
o-toluic	111
p-toluic	104
Phenylacetic	4
2,4 and/or 2,5 Dimethylbenzoic[1]	683
2,6 Dimethylbenzoic	25
m-methylphenylacetic	225
p-methylphenylacetic	117
3,4 Dimethylbenzoic	60
2,4,6 Trimethylbenzoic	142

[1] These isomers were not separated chromatographically.

The distribution of bicarbonate and $\delta^{13}C$ of total CO_2 (in per mil (‰)) for July 1990 is shown in figure 5. The heaviest $\delta^{13}C$ values were found in the zone of highest bicarbonate concentrations. In July 1990, the pH of the ground water ranged from a maximum of 6.11 at a depth of 15.5 ft to 4.65 at depths of 18 and 22 ft. Uncontaminated ground water in the perched water zone typically contains dissolved oxygen (0.17 mM), nitrate (0.64 mM), and sulfate (0.25 mM), very little bicarbonate (0.04 mM), no measurable iron, and has a pH of 4.73 (Baedecker and others, 1991, this Proceedings). The $\delta^{13}C$ of CO_2 in background water in the perched and water table aquifers ranged from -28 to -26 ‰.

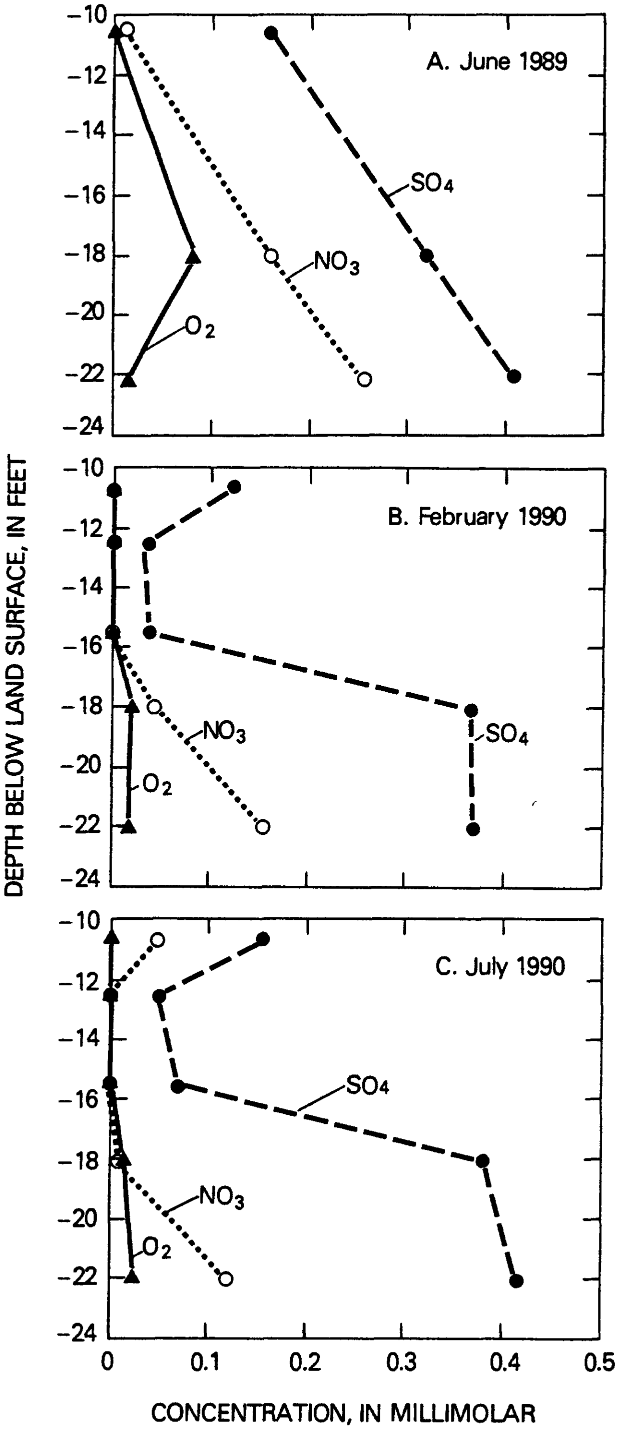

Figure 3. Concentrations of electron accepting species (millimolar), oxygen, nitrate and sulfate, as a function of depth below land surface at location X in June 1989, February 1990, and July 1990.

DISCUSSION

The distribution of hydrocarbons in ground water at this site indicates that the low-molecular-weight aromatic hydrocarbons dissolve due to their high solubilities.

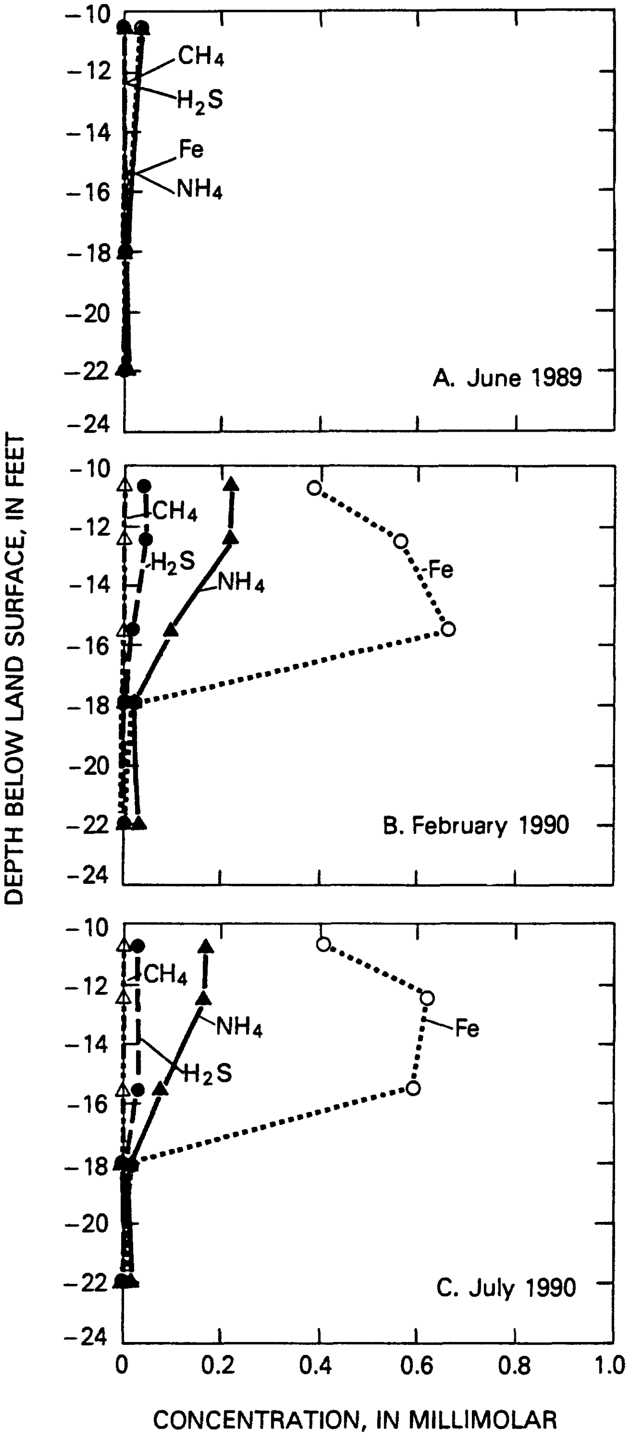

Figure 4. Concentrations of reduced chemical species (millimolar), ammonium, hydrogen sulfide, ferrous iron and methane as a function of depth below land surface at location X in June 1989, February 1990, and July 1990.

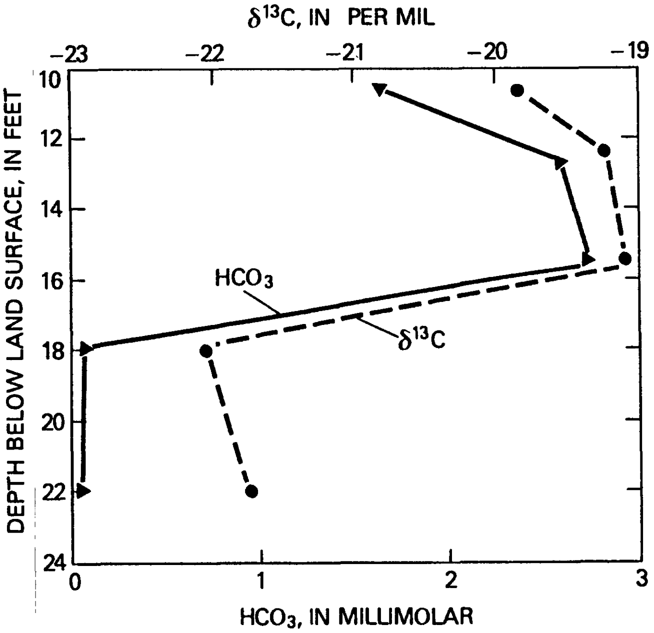

Figure 5. Concentration of bicarbonate (millimolar) and the $\delta^{13}C$ of total inorganic carbon (per mil) as a function of depth below land surface at location X in July 1990.

The low-molecular-weight aliphatic hydrocarbons ($<C_6$) could have volatilized or been microbially degraded in the unsaturated zone. Aliphatic hydrocarbons greater than C_6 have low aqueous solubilities and may sorb onto the aquifer sediment, be microbially degraded, or remain in the gasoline.

Anoxic conditions developed in ground water near the gasoline source as oxygen was consumed during the aerobic degradation of hydrocarbons. Under these conditions, anaerobic degradation reactions became important. The presence of organic acids, which are intermediates in the degradation of hydrocarbons, in the contaminated water indicates that microbial degradation of the hydrocarbons occurred. Several investigators have reported the presence of organic acids in anoxic ground water downgradient from landfills and hydrocarbon spills (Baedecker and Back, 1979; Reinhard and others, 1984; Goerlitz and others, 1985; Cozzarelli and others, 1990). The highest concentrations of organic acids are found where anaerobic microbial degradation processes are dominant. The aromatic hydrocarbon, 1,2,4 trimethyl benzene (1,2,4 tmb), was one of the more abundant alkylbenzenes in this zone, and the predominant organic acid found, 2,4 or 2,5 dimethyl benzoic acid, (table 1) could result from the oxidation of one of the methyl groups of 1,2,4 tmb. Other sources for the organic acids, aside from the degradation of gasoline hydrocarbons, such as decomposition of natural organic material present in the aquifer, are unlikely to be important at this site. The amount of natural soil-organic matter is very low, and the concentration of dissolved organic carbon in uncontaminated ground water at this site is less than 2 mg/L.

Geochemical data indicate that nitrate, iron, and sulfate reduction are important biogeochemical processes in the shallow ground water at this site (figs. 3 and 4). Ammonia, ferrous iron, and sulfide are the reduced end products of anaerobic hydrocarbon degradation. Laboratory experiments of Mills and Randall (1991, this Proceedings) verified the presence of anaerobic bacteria in ground water at this site. Such bacteria could grow on gasoline hydrocarbons with the use of alternate electron acceptors (NO_3 and SO_4). The geochemical data suggest that competing redox reactions occur simultaneously and, thus, Eh is controlled by several reactions rather than one predominant reaction. Although thermodynamics predict that nitrate and iron reduction should cease before sulfate reduction would occur, these competing degradative processes appear to occur simultaneously in the 12.5- to 15.5-ft section of the aquifer. In the water table aquifer (below a depth of 18 ft), oxygen is available at low levels and, thus, aerobic degradation may be an important microbial degradation process. The lack of any appreciable concentrations of reduced chemical species in this zone (fig. 4) support the hypothesis that anaerobic degradation is limited. The small amount of ammonia and the depletion of nitrate at a depth of 18 ft indicate that nitrate reduction, possibly by facultative anaerobic bacteria, may be occuring on a small scale or in microenvironments. Other possible sources of ammonia in contaminated aquifers are from the degradation of nitrogen-containing organic compounds. The contaminant at this site, gasoline, would not contain a significant organic nitrogen fraction. However, the importance of organic nitrogen from the soil zone or from the recycling of inorganic nitrogen into the organic nitrogen pool by bacteria is unknown.

Geochemical reactions that change over time most likely are the result of changes in the hydrologic conditions at this site. Oxygen, nitrate, and sulfate in the shallow perched water (10.7-ft depth) is supplied by vertical recharge from precipitation events, whereas at the deeper depths, these electron acceptors are supplied by horizontal movement of ground water from recharge areas upgradient of the site as well as vertical recharge from the perched water zone. During June 1989, the water table was 16 ft below land surface and the sampling probe at a depth of 15.5 ft was dry. In February and July 1990, the water table was higher, about 15 ft below land surface, and the sediment at a depth of 15.5 ft was saturated. The higher concentrations of oxygen and nitrate and the lack of any reduced chemical species at a depth of 18 ft in June 1989 compared to throughout 1990 indicates that these electron acceptors were not completely utilized in microbially mediated degradation reactions. The low concentration of hydrocarbons at this depth in June 1989 (fig. 2) was insufficient to cause depletion of O_2 and NO_3. An extensive unsaturated zone between the water table and the perched water during the dry period (June 1989) limits vertical mixing of the perched water and water table aquifer. The lack of significant recharge through the more contaminated shallow zone to the water table during dry periods limits the supply of hydrocarbons for degradation.

The $\delta^{13}C$ of inorganic carbon (fig. 5) indicates that the CO_2 pool is heavier in the zone of greatest contamination relative to background values. The heaviest $\delta_{13}C$ values are also in the zone with the highest bicarbonate concentrations. This inorganic carbon comes from the complete mineralization of organic material to CO_2 and H_2O by microorganisms. Because methane concentrations are low at this site, it seems unlikely that the fractionation of carbon by methanogens is an important process. The fractionation of stable carbon isotopes in pristine and contaminated ground-water environments is well documented (Games and Hayes, 1976, 1977; Barker and Fritz, 1981). Methanogenesis, an anaerobic microbial process, results in a large fractionation of carbon, whereby methane is depleted in ^{13}C and CO_2 is enriched in ^{13}C. However, fractionation of carbon by other unidentified processes may cause enrichment of ^{13}C in the inorganic carbon pool. The heavier $\delta^{13}C$ values may also result from the selective degradation of organic compounds that have a heavier isotopic composition than the natural soil carbon. The organic acids identified in the anoxic ground water would be ultimately transformed into end products, such as CO_2 and water. The isotopic composition of these organic acids and the contribution that the acids make to the production of inorganic carbon is largely unknown.

Examination of the geochemical data using a computerized equilibrium speciation model, WATEQF (Plummer and others, 1976), reveals the potential for significant changes in aquifer minerals due to the degradation of hydrocarbons. These changes may be particularly important in the shallow regions of the contaminated area (less than 16 ft below land surface). In uncontaminated ground water at this depth, all secondary minerals described below were undersaturated, emphasizing the extremely dilute nature of these waters and the lack of any significant carbonate minerals. The high concentrations of iron, bicarbonate, and sulfide produced during the degradation of hydrocarbons near the gasoline source produces ground water that is supersaturated with respect to iron sulfide, iron carbonate and iron and aluminum oxyhydroxides. Pyrite (FeS_2), mackinawite (FeS) and amorphous iron sulfide (FeS) are supersaturated in ground water at depths of 10.7 to 15.5 ft. Precipitation of iron-sulfide minerals has been shown to occur in contaminated environments (Hearn and others, 1986) and is associated with microbial sulfate reduction. Precipitation of these minerals may limit the concentrations of sulfide in the ground water. Siderite ($FeCO_3$) may also be forming in a narrow zone of the aquifer (12.5-15.5 ft deep) in which the ground water is slightly supersaturated with repect to siderite. Ground water is also supersaturated with respect to magnetite (Fe_3O_4) in this zone. Magnetite formation by iron reducing bacteria has been demonstrated in laboratory experiments (Bell and others, 1987; Lovley and others, 1987) and has been suggested as the mechanism for magnetite deposits found near hydrocarbon deposits (Elmore and others, 1987; McCabe and others, 1987). The increase in pH resulting from organic degradation reactions decreases the solubility of aluminum hyroxide minerals. In the shallow contaminated zones, ground water is supersaturated with respect to gibbsite and aluminum concentrations are less than half of what they are in uncontaminated water at this depth. Precipitation of gibbsite or formation of clay minerals such as kaolinite may control the aluminum concentrations in this part of the aquifer. Further work at this site will involve examination of the aquifer solids to assess the importance of the degradation of hydrocarbons on secondary-mineral formation.

SUMMARY

The ground-water chemistry in a vertical section of the aquifer near the gasoline spill showed that the aquifer was severely affected by the hydrocarbon contaminants. The reactions that control the distribution of hydrocarbons and organic acids are microbially mediated oxidation-reduction reactions. Significant geochemical alterations of the ground-water chemistry and aquifer solids occur because of these reactions. The highest concentration of dissolved hydrocarbons and organic acids are found in the zone 12.5 to 15.5 ft below land surface where nitrate reduction, iron reduction, and sulfate reduction are important degradation processes. This zone is characterized by the depletion of oxygen, nitrate, and sulfate; an increase in pH, bicarbonate, ammonium, ferrous iron, and hydrogen sulfide; and enrichment of the ^{13}C of inorganic carbon. In deeper zones (18-22 ft below land surface), aerobic degradation and, to a lesser extent, nitrate reduction occur. The release of reduced chemical species and increases in pH and bicarbonate concentrations as a result of the microbial degradation of the hydocarbons and organic acids may produce discrete zones where secondary minerals such as iron sulfide, iron carbonate, and iron and aluminum oxyhydroxides may precipitate.

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ABUNDANCE AND DISTRIBUTION OF MICROBIAL GUILDS IN A SUBSURFACE PLUME OF GASOLINE CONTAMINATION AT GALLOWAY TOWNSHIP, NEW JERSEY

By Aaron L. Mills[1] and Susan E. Randall[1]

ABSTRACT

The distribution of total, viable, and hydrocarbon-degrading microorganisms in the sediments and ground waters of a gasoline-contaminated site in Galloway Township, New Jersey, was determined in May and July 1990. Total bacteria (determined by acridine orange direct counts) were more uniformly distributed with depth than total viable microbes (aerobic plate counts) and the hydrocarbon utilizers (aerobic cultural counts). These organisms were most abundant at the surface of soil and near the surface of perched or regional water tables. The presence of microbes that could grow under anaerobic conditions at the expense of the hydrocarbon and alternative inorganic terminal electron acceptors (nitrate, sulfate, and ferric iron) was consistent with the presence of products of anaerobic microbial respiration in samples from the same sites.

INTRODUCTION

Hydrocarbon contamination of soils, water, and subsurface environments is characterized by changes in the structure of the microbial community from that which existed in the pre contamination state (see, for example, Colwell and others, 1978). The shifts may be manifested as an increase in the abundance of some organisms as a result of their ability to use the hydrocarbons or intermediate breakdown products as a source of carbon and energy. Other alterations arise as a result of toxic effects of some hydrocarbon compounds on other microbes that cause a decrease in the abundance of those organisms. These shifts may be described by an alteration in the relative abundance of certain microbial species (a description that provides little useful information) or by an alteration in the relative abundance of certain microbial guilds (groups of organisms that possess similar functional abilities).

Increases in the number of organisms capable of using hydrocarbons relative to the total microbial abundance has long been associated with hydrocarbon contamination. Elimination of the contamination carries the implicit assumption that the number of hydrocarbon degraders should then be expected to decline over time. The latter point is of importance in consideration of bioremediation alternatives for the cleanup of hydrocarbon contamination. If an organism or suite of organisms (natural or engineered) can be introduced to a contaminated area, an implicit requisite is that the introduced organisms disappear when the cleanup has been effected and the contamination has been eliminated. This paper describes the results of a study to examine the abundance of general heterotrophic (organotrophic) bacteria and hydrocarbon utilizing bacteria in the proximity of gasoline contamination from a leaking storage tank at the U.S. Geological Survey research site in Galloway Township, N.J.

An additional consideration for the study deals with the activity of microbes in the zone of contamination. Measurement of oxygen (O_2) and carbon dioxide (CO_2) concentrations in the contaminated area indicate a zone of anaerobiosis centered on the tank site (highest contamination) (Baehr and others, 1991, this Proceedings). The absence of O_2 near the center of the plume suggest that the active hydrocarbon degraders in this location are aerobes. Oxygen depletion and continued microbial action create unique geochemical zones associated with the contaminant plume. Alternative electron acceptors are consumed in order of preference by the adapting microbial populations (Atlas and Bartha, 1987). In organic contamination from landfills, the following scenario has been suggested (Baedecker and Back, 1979):

(1) Oxidation of organic compounds with oxygen acting as the electron acceptor to form bicarbonate (HCO_3^-), nitrate (NO_3^-), and sulfate (SO_4^{2-}).
(2) After free O_2 is depleted, NO_3^- is reduced to N_2 and iron and manganese are solubilized.
(3) SO_4^{2-} is reduced (to hydrogen sulfide [H_2S])
(4) Organics become the source of electron acceptors during fermentation yielding methane (CH_4) and ammonia (NH_4^+).

Studies of subsurface microbial abundance within landfill leachate plumes show a similar pattern to that indicated by the geochemical composition. The greatest geochemical changes are seen closest to the organic contaminants. As the distance from the contaminant increases and the concentration of organic compounds decreases, the number of organisms (as colony-forming units on an enumeration medium) decreases (Harvey and others, 1984).

Leaking underground tanks pose a somewhat difficult problem for the microbes. Hydrocarbon disappears from the soil surface much more rapidly than the subsurface (Song and Bartha, 1990). Subsurface leaks are initially restricted to the unsaturated zone with water serving as a barrier to the less dense hydrocarbon. With slow gas exchange, the oxygen becomes quickly depleted, thus limiting effective microbial attack.

If there is an increase in the microbial abundance to take advantage of the increased carbon/energy source, where does the increase occur? Is the greatest microbial density seen in the area of the highest concentration of carbon source, or above the source closer to the surface and, thus, to oxygen?

METHODS

Total microbial abundance, abundance of hydrocarbon degraders, and presence of certain anaerobic guilds were

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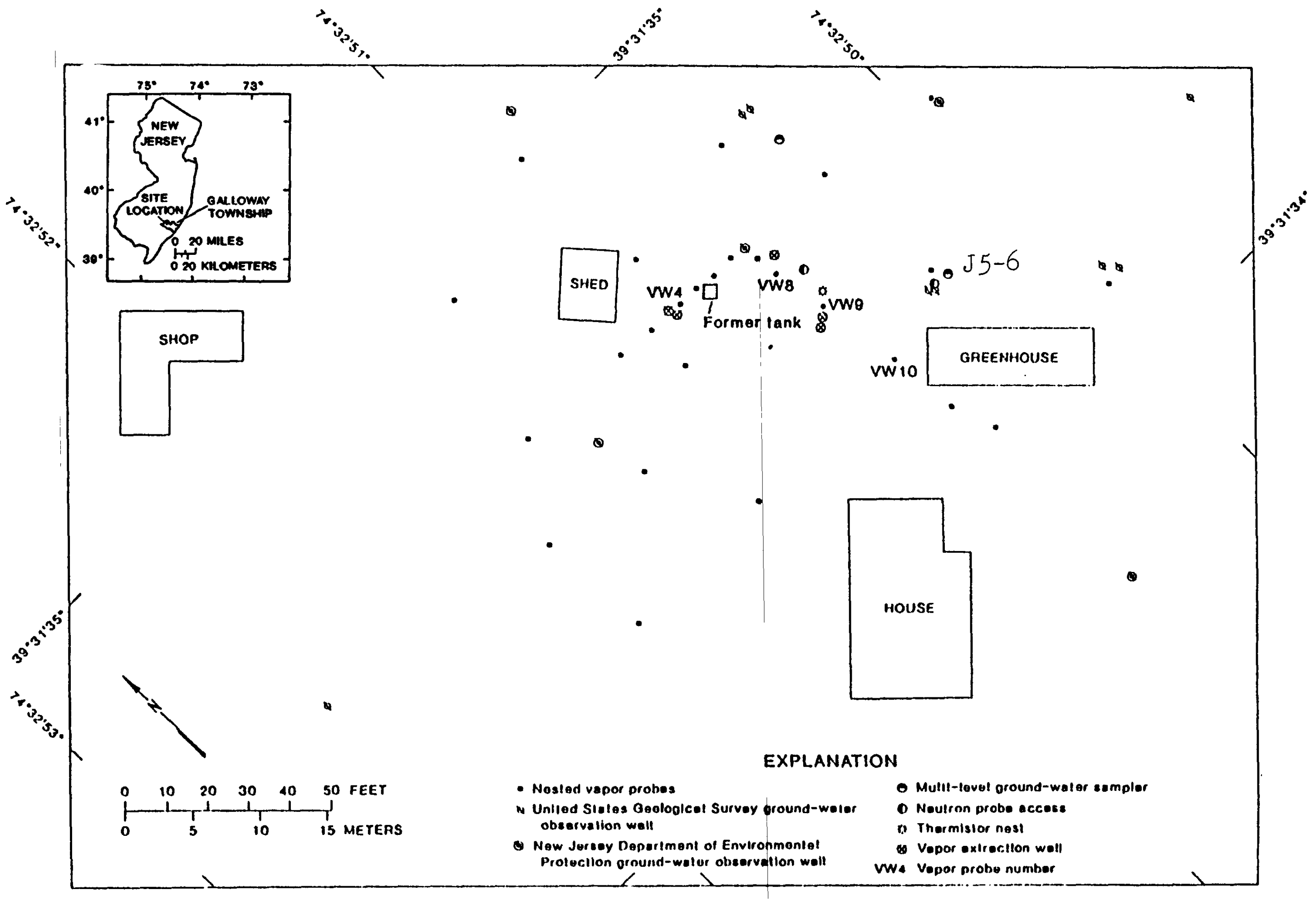
74°32'51"
39°31'35"
74°32'50"
74°32'52"
39°31'34"
39°31'35"
74°32'53"
75°
74°
73°
41°
40°
39°
NEW JERSEY
SITE LOCATION
GALLOWAY TOWNSHIP
0 20 MILES
0 20 KILOMETERS
SHOP
SHED
VW4
VW8
VW9
Former tank
J5-6
GREENHOUSE
VW10
HOUSE
N
0 10 20 30 40 50 FEET
0 5 10 15 METERS
EXPLANATION
Nested vapor probes
United States Geological Survey ground-water observation well
New Jersey Department of Environmental Protection ground-water observation well
Multi-level ground-water sampler
Neutron probe access
Thermistor nest
Vapor extraction well
VW4 Vapor probe number

Figure 1. Galloway Township site showing location and designation of the samplers and wells.

evaluated in sediment and water samples taken prior to the proposed soil venting operation. Core samples were taken at intervals from vapor wells 9, 4, 8 and multilevel water sampler J5-6 (fig. 1). Two samplings were done in 1990, one in May and another in July.

Microbial Abundance

The abundance of several classes of bacteria was determined. The total number of bacterial cells present was measured by the Acridine Orange Direct Count (AODC) method. Results from this method provide a view of the total number of bacteria present in a sample, although nothing can be said about bacterial activity, ability, or even viability. Because all culture media are selective for some organisms over others, AODC gives the best representation of the absolute number of bacteria present. Total heterotrophic counts (TVC) represent the best index of the total number of organisms present that use organic molecules as a source of carbon and energy. Because no culture medium is truly nonselective, this technique invariably yields results that are an underestimate of the true value. Hydrocarbon-degrader counts (HC) represent those organisms capable of growth using the contaminant (or analogous compounds) as the sole source of carbon and energy. Although all three microbial groups (total, heterotrophic, and hydrocarbon utilizing) might be expected to increase as a result of hydrocarbon contamination, the organisms enumerated by the HC method should show the greatest enrichment.

Acridine Orange Direct Counts

Approximately 0.1 mL (milliliter) of each of the sediment samples were fixed in the field in 20 mL of formaldehyde (5 percent) and kept under refrigeration until they were analyzed. In the lab, blended samples were stained with acridine orange and filtered through irgalin black-dyed Nuclepore filters, and the cells were counted using the 100x objective for 5 to 10 fields, (Hobbie and others, 1977).

Viable Cell Counts

Sediment dilutions of 10^{-3}, 10^{-4}, 10^{-5}, and 10^{-6} were plated onto a modified (1:20 dilution) peptone-tryptose-yeast extract- glucose (PTYG) medium (Balkwill and Ghiorse, 1985). This medium has been shown to be excellent for the recovery of subsurface microorganisms. Colonies were counted after incubation at approximately 26 °C (degrees Celsius) for 5 days.

Abundance of Hydrocarbon Degraders

Colony-forming units were determined for hydrocarbon degraders from sediment dilutions of 10^{-2}, 10^{-3}, 10^{-4}, and 10^{-5} plated onto an agar-solidified artificial ground water (AGW) medium with a gasoline saturated filter paper (Calomiris and others, 1977) included in the lid of the petri dish to provide similar carbon/energy source availability for the microorganisms as found in the vadose zone. AGW contains, $CaCO_3$, 1.203 g/L (gram per liter); $NaHCO_3$, 0.164 g/L; $(NH_4)_2HPO_4$, 0.004 g/L; $MgCl_2$, 0.005 g/L; K_2HPO_4, 0.005 g/L; $MnCl_2$, 0.0015 g/L; Co, Cu, Zn, trace (one drop atomic absorption spectrophotometry standard solutions).

The presence of microbes capable of using gasoline as a sole source of carbon and energy under anaerobic conditions in the presence of the alternative electron acceptors, NO_3^-, SO_4^{2-} and Fe^{3+} was determined in the July sampling for waters from the saturated zones of the profiles. Anaerobic crimp vials flushed with N_2 containing AGW and amended with various alternative electron acceptors (0.1 g/L of KNO_3, K_2SO_4, or $Fe(OH)_3$ (Mills and Bell, 1986) and 0.1 mL of 1:1:1 mixture of benzene: toluene:xylene (BTX) were inoculated with 1-mL water samples taken in July from the saturated zone penetrated by vapor wells 4 and 9 and sampler J5-6. Samples were incubated at 17 °C for approximately 4 weeks when growth was determined by the appearance of visible turbidity.

RESULTS

The cultural methods used recovered a variable part of the organisms enumerated by the direct counts (figs. 2 and 3). For example, in the May 1990 sampling, the AODC in samples from VW4 ranged from about 2×10^8 to 8×10^8 cells/g (cells per gram) of sediment, whereas the number of viable cells (TVC) spanned a much larger (proportionate) range: from 1×10^5 to 5×10^7 cells/g (fig. 1). Furthermore, AODC values tended to be relatively constant with depth in all samples, whereas TVC values generally decreased with depth, but increased again near the surface of the water table. For those samples in which HC were determined, the numbers of such organisms were high, commonly approaching the values observed for the TVC.

In the July sampling, the general patterns observed in May were still evident, but the number of HC organisms fequently exceeded the number of TVC recovered (see

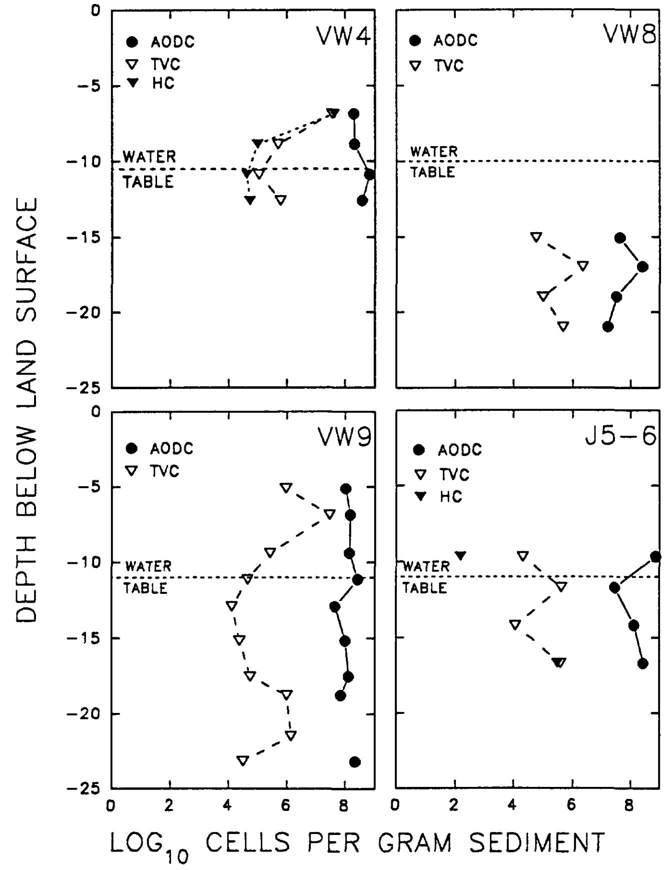

Figure 2. Distribution of bacteria in vapor wells 4 (VW4), 8 (VW8), 9 (VW9), and multilevel sampler J5-6 in May 1990. Symbols refer to acirined orange direct counts (AODC), total viable counts (TVC), and hydrocarbon utilizer counts (HC).

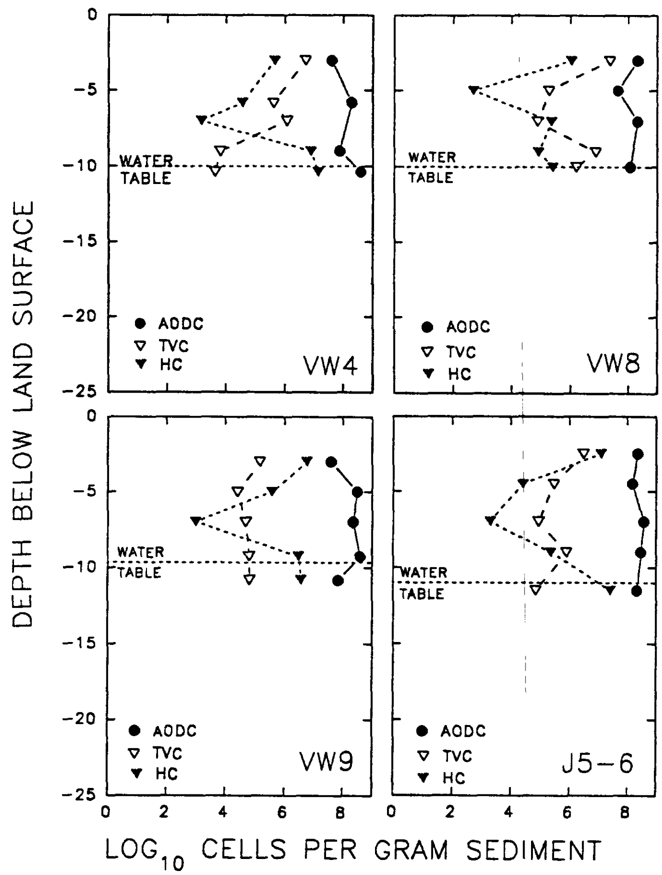

Figure 3. Distribution of bacteria in vapor wells 4 (VW4), 8 (VW8), 9 (VW9), and multilevel sampler J5-6 in July 1990. Symbols refer to acridine orange direct counts (AODC), total viable counts (TVC), and hydrocarbon utilizer counts (HC).

fig. 2). This phenomenon is not an uncommon one, because a location heavily contaminated with hydrocarbons may contain a larger number of microbes capable of utilizing the contaminants than the number that are capable of using the ingredients provided in the medium used for the TVC enumerations.

In July, the distribution of anaerobes indicated the presence of NO_3^--reducing, SO_4^{2-}-reducing, and possibly Fe-reducing bacteria in the saturated zones of each of the sites sampled (table 1). That finding is supportive of the results of Baedecker and others (1991, this Proceedings) who reported the presence of products of anaerobic metabolism in the saturated zone at the site.

Table 1. *Presence of anaerobic organisms in water samples collected at the Galloway Township site in July 1990. Depths are given in feet below land surface*

Sample site	Depth	SO_4^{2-}	NO_3^-	Fe^{3+}
VW9	10.7	+	+	-
	12.5	+	+	-
	15.5	+	+	+
	22	+	+	+
J5-6	20.3	-	-	-
	23.3	+	-	-
	24.7	+	+	-
VW4	10.6	+	-	-

DISCUSSION

The observation of relatively stable AODC values with depth, compared with TVC results that fluctuate is reasonable for this site because of the gasoline contamination at depth in the profile. The high numbers of gasoline degraders is expected given the long time period of contamination (up to 40 years) during which enrichment could easily occur and given the currently abundant supply of hydrocarbon in the vadose zone and at the surface of the water table.

The enumeration technique used for the HC organisms selected for those microbes that could use the gasoline under aerobic conditions. The high numbers obtained supports the observation of low O_2 and high CO_2 seen in the vadose zone; the aerobic microbes undoubtedly removed the oxygen during oxidation of the carbon in the gasoline to CO_2.

The observation that microbes were present that could grow anaerobically at the expense of the gasoline analog, benzene- toluene-xylene (BTX), using one of the alternative electron acceptors, may explain the observed accumulation of products of anaerobic respiration in the saturated zone at the site.

Further work will examine seasonal differences in the distribution of all of the organisms and will examine the alterations in the relative abundance of the various microbial guilds upon completion of the venting procedures underway presently at the Galloway Township site.

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USE OF A MULTILEVEL SAMPLER TO DETERMINE VERTICAL CONCENTRATION GRADIENTS OF VOLATILE AROMATIC HYDROCARBONS IN GROUND WATER, GALLOWAY TOWNSHIP, NEW JERSEY

By Jacob Gibs[1], G. Allan Brown[1], and Kenneth S. Turner[1]

ABSTRACT

Observation wells are a standard means for gaining access to ground water in order to determine its chemistry. Evidence indicates that observation wells can produce a biased sample when analyte concentrations are not uniform in the vicinity of the well screen, however. This paper demonstrates that use of a wire-wound screen integrates the water chemistry as a function of depth in ground water contaminated by leaded gasoline at Galloway Township, New Jersey. Two multiport samplers were designed, built, and installed 55 feet apart. The multiport samplers were used to collect seven independent samples within the screened zone to simulate a 5-foot-long, 2.375-inch-outside-diameter conventional wire-wound screen. Samples collected with the two multiport samplers show that a conventional 5-foot-long well screen that integrates contaminant concentrations over its length can result in a contaminant concentration that is as little as 28 percent of the maximum concentration observed in the multiport sampler.

INTRODUCTION

The presence of a nonaqueous phase organic contaminant in ground water can cause large changes in the aqueous concentration of the contaminants with depth. The problem of obtaining representative water samples to delineate the vertical changes in concentration requires the use of a sampling device other than conventional observation wells.

Conventional observation wells are ideally designed to permit collection of a water sample from the part of aquifer within the screened interval of the well; this sample is a depth-integrated sample. This depth-integrated nature of water samples from conventional wells is not suited to the investigation of variations in water chemistry with depth. The use of nests of wells with short screens has two disadvantages: The installation is difficult and costly, and the interpretation of the change in concentration with depth is complex because the screens are not at the same areal location. The importance of variations in areal location of wells in a nest decreases as the scale of the contamination increases.

Multiport samplers are easier and less costly to install than nested wells. A multiport sampler developed by Pickens and others (1978) has been used successfully, with minor modifications, at the Cape Cod, Mass., Toxic-Substances Hydrology research site (LeBlanc and others, 1987). The multiport device used by LeBlanc and others (1987) consists of a structural support pipe of polyvinyl chloride (PVC) with 15 polyethylene tubes, each with a 0.25-in. (inch)-outside diameter (OD), inside the PVC pipe. Each of the polyethylene tubes protrudes through a hole in the PVC pipe. This hole is screened with nylon fabric over a vertical distance of 0.1 ft (foot). Installation was accomplished by one of two methods: by conventional hollow-stem augering to the desired depth, installing the multiport sampler, and withdrawing the augers; or by driving open-ended, flush-jointed drive casing (size BW or NXWL) to the desired depth, washing sediment out, installing the multiport sampler, and withdrawing the flush-jointed drive casing.

The multiport sampler described above has several limitations. For example, it samples water in an asymmetrical manner about the PVC structural support pipe. Also, the installation method allows the aquifer sediment to collapse against the support pipe, which may change the local hydraulic conductivities of the aquifer around the hole. Another important limitation is that the multiport sampler can be sampled only with suction-lift pumps, whereas conventional, large-diameter monitoring wells can be sampled by using either suction-lift or positive-displacement pumps. In addition, the multiport samplers used by Pickens and others (1978) and LeBlanc and others (1987) are made of materials not among those recommended by Barcelona and others (1983) for sampling trace aqueous concentrations of organic compounds; the preferred materials are stainless steel, polytetrafluoroethane, and glass.

This paper describes the design and installation of a new multiport drive-point sampler used to obtain water samples containing volatile aromatic hydrocarbons from gasoline-contaminated ground water in Galloway Township, N.J. The site is a current U.S. Geological Survey (USGS) Toxic-Substances-Hydrology research site with an existing network of 13 ground-water observation wells. The multiport sampler was designed to study the compositing of water samples over the length of a well screen. This could be done only by duplicating as closely as possible flow to a conventional water-quality observation well with a wire-wound screen during sampling. The paper describes (1) the design and installation of the multiport sampler and (2) the results of water-quality sampling to document the presence of variations in the concentration of volatile aromatic hydrocarbons with depth.

METHODS

Sampler Construction

The multiport sampler used in this study is constructed entirely of 304 stainless steel and has an OD of 2.375 in. The sampler was designed in conjunction with, and was built at, the USGS Hydrologic Instrumentation Facility (Jelinski, 1990). The sampler consists of a drive point at the base,

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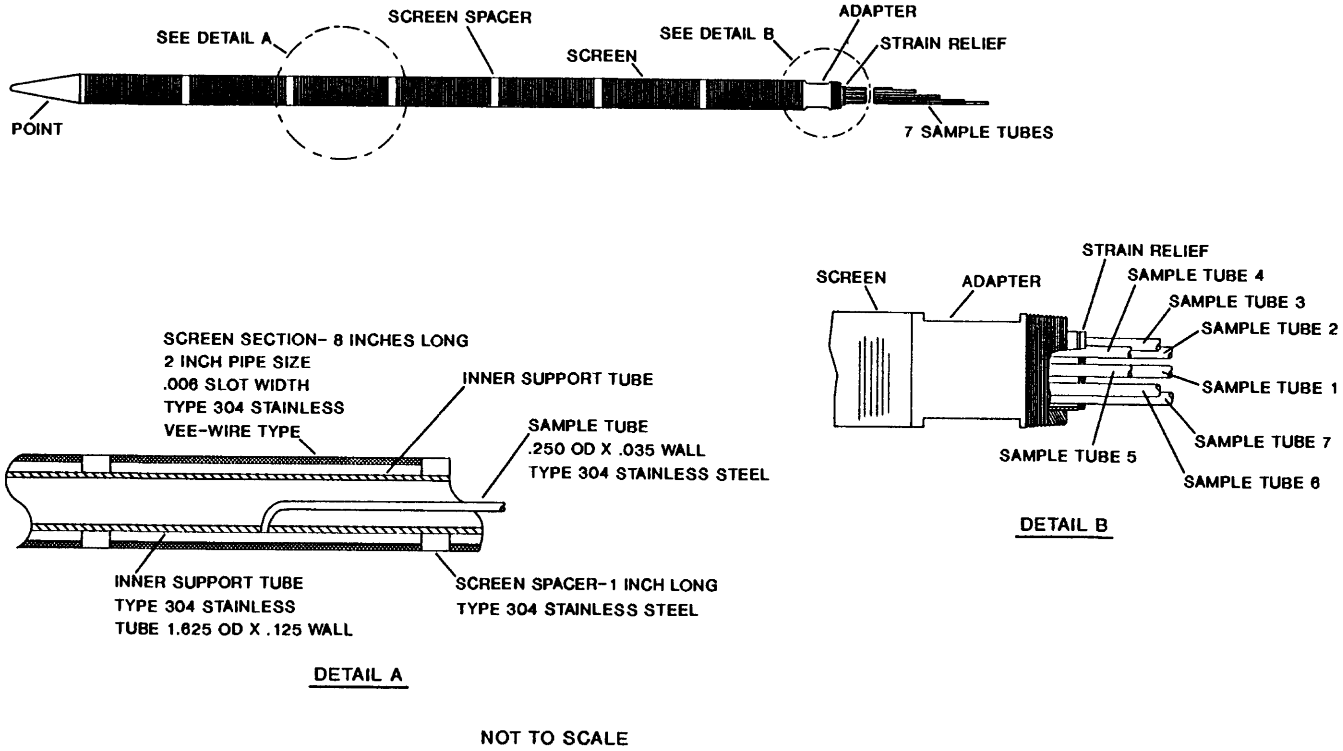
SCREEN SPACER
SEE DETAIL A
SCREEN
SEE DETAIL B
ADAPTER
STRAIN RELIEF
POINT
7 SAMPLE TUBES
SCREEN SECTION- 8 INCHES LONG
2 INCH PIPE SIZE
.006 SLOT WIDTH
TYPE 304 STAINLESS
VEE-WIRE TYPE
INNER SUPPORT TUBE
SAMPLE TUBE
.250 OD X .035 WALL
TYPE 304 STAINLESS STEEL
INNER SUPPORT TUBE
TYPE 304 STAINLESS
TUBE 1.625 OD X .125 WALL
SCREEN SPACER-1 INCH LONG
TYPE 304 STAINLESS STEEL
DETAIL A
SCREEN
ADAPTER
STRAIN RELIEF
SAMPLE TUBE 4
SAMPLE TUBE 3
SAMPLE TUBE 2
SAMPLE TUBE 1
SAMPLE TUBE 7
SAMPLE TUBE 6
SAMPLE TUBE 5
DETAIL B
NOT TO SCALE

Figure 1. Drawing of multiport sampler showing construction details. (Modified from Jelinski, 1990).

seven screen sections separated by 1-in.-long spacers, and a pipe adapter at the top (fig. 1). Each screen section is 8 in. long and is constructed of wire-wound screen with a 0.006-in. slot width. The screens are held in place and are separated from adjacent sections by the 1-in.-long spacers. Inside each screen is a 1.625-in.-OD support pipe which runs along the length of the sampler. Within each screen section a 0.25-in.-OD sample tube penetrates the support pipe. The open space between the support pipe and the screen allows water to be drawn through the screen over its length and circumference. At the top of the sampler is a 2-in.-long male pipe-thread adapter and a support disc with eight holes for the 0.25-in.-OD sample tubes and a pressure-equalization hole. The seven sample tubes run up the center of the support pipe and through the top of the sampler.

The multiport sampler is attached to nominal 2-in.-inside diameter (ID) schedule 80 steel riser pipe extending from the top of the sampler to land surface. Inside this riser pipe is a bundle of seven fluorinated ethylene propylene (FEP) tubes with a 0.375-in. OD and a 0.25-in. ID. The FEP tubes slide over the upper end of the 0.25-in.-OD stainless-steel tubes of the multiport sampler and are sealed with two stainless-steel hose clamps. These FEP tubes are bundled within 1.5-in.-OD polyethylene shrink tubing. The FEP tubing extends from the top of the stainless-steel tubing of the multiport sampler to land surface and conveys the sample water from a specified depth or zone to the surface.

Sampler Installation

The installation procedure described below was developed by trial and error during a previous installation at the Galloway Township site. During the previous installation, the screens of the multiport sampler had become plugged as the sampler was driven through a series of interbedded sand and clay layers before reaching the water table. In order to minimize the possibility of plugged screens, this installation was accomplished by using a hollow-stem-auger drill rig to auger an 8.5-in. hole to about 17.5 ft below land surface. The 4.25-in.-ID hollow-stem auger was then used as a temporary casing to prevent the hole from collapsing during the rest of the installation procedure.

After the hole was augered to 17.5 ft, nominal 1.5-in.-ID schedule 80 steel pipe was lowered into the augers and was driven from 17.5 ft to 30 ft and 33 ft below land surface for samplers 5-6 and 7-8, respectively. A natural-gamma-ray borehole-geophysical log (gamma log) was then run inside the nominal 1.5-in.-ID pipe to determine the depth of clay lenses at each location. As shown in figures 2 and 3, both multiport samplers were placed in sand below clayey layers as determined from the gamma logs and split-spoon cores from wells less than 10.3 ft from the samplers. Both samplers were placed at a depth of less than 25.5 ft because slightly elevated counts on the gamma logs indicated the presence of a small amount of clay in the formation at a depth greater than 26.5 ft. After logging, the nominal 1.5-in.-ID pipe was withdrawn from the ground.

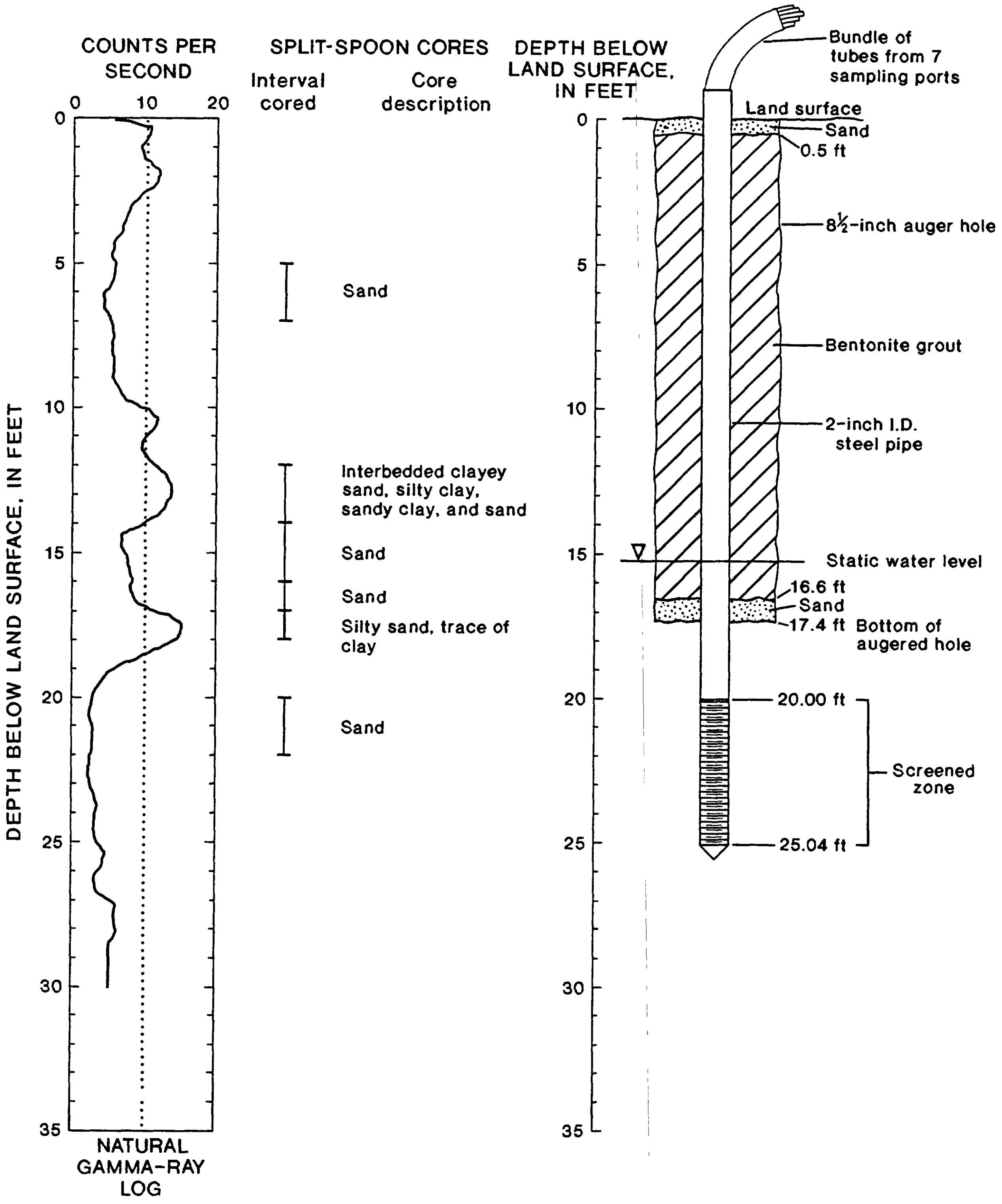
COUNTS PER SECOND
0
10
20
SPLIT-SPOON CORES
Interval cored
Core description
DEPTH BELOW LAND SURFACE, IN FEET
0
5
10
15
20
25
30
35
Sand
Interbedded clayey sand, silty clay, sandy clay, and sand
Sand
Sand
Silty sand, trace of clay
Sand
NATURAL GAMMA-RAY LOG
DEPTH BELOW LAND SURFACE, IN FEET
Bundle of tubes from 7 sampling ports
Land surface
Sand
0.5 ft
8½-inch auger hole
Bentonite grout
2-inch I.D. steel pipe
Static water level
16.6 ft
Sand
17.4 ft Bottom of augered hole
20.00 ft
Screened zone
25.04 ft

Figure 2. Natural gamma-ray log of test hole for sampler 5-6 and diagram of sampler 5-6 installation. (Split-spoon cores were collected from a corehole 4.8 feet from the sampler location.)

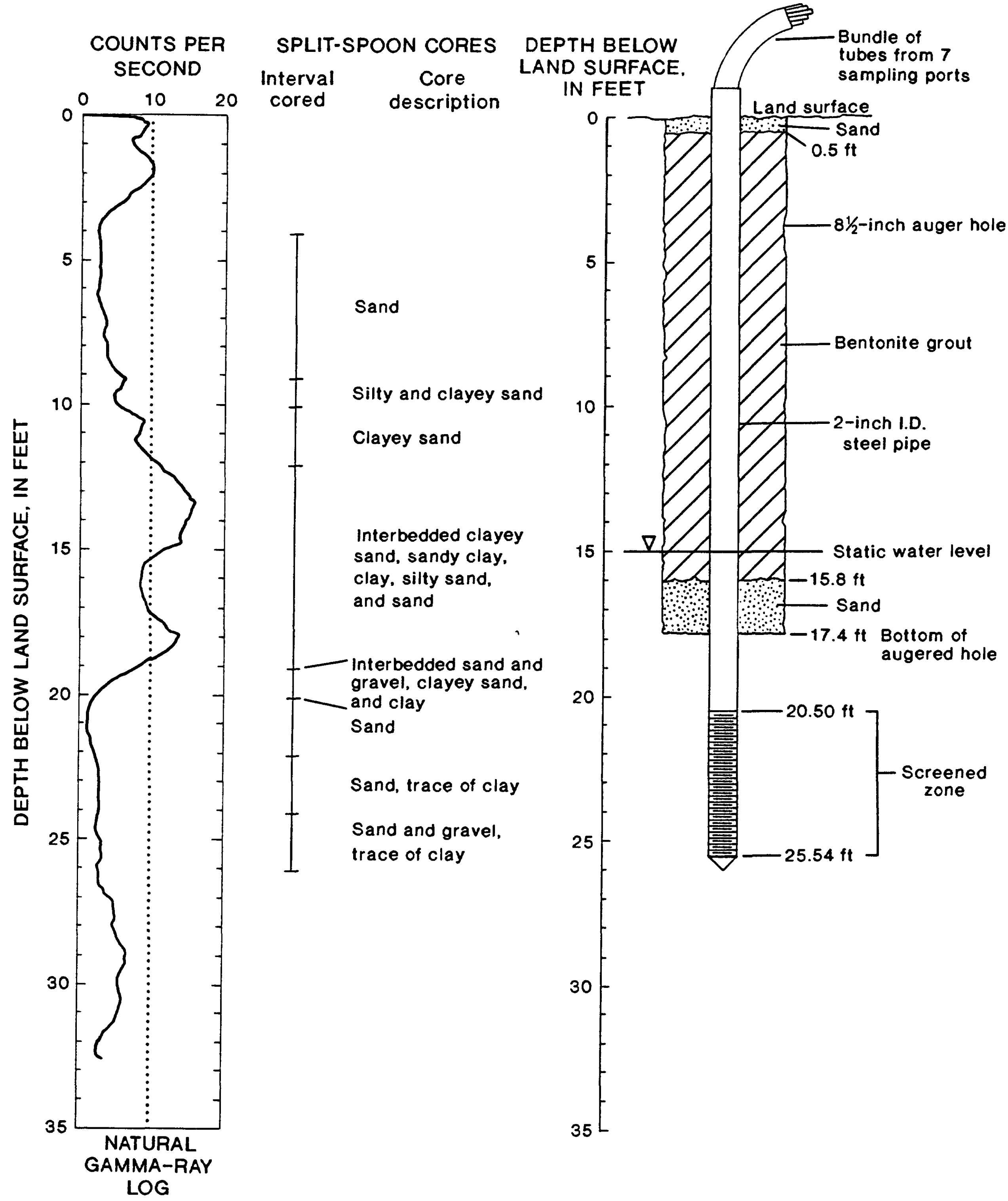
COUNTS PER SECOND
0
10
20
DEPTH BELOW LAND SURFACE, IN FEET
0
5
10
15
20
25
30
35
NATURAL GAMMA-RAY LOG
SPLIT-SPOON CORES
Interval cored
Core description
Sand
Silty and clayey sand
Clayey sand
Interbedded clayey sand, sandy clay, clay, silty sand, and sand
Interbedded sand and gravel, clayey sand, and clay
Sand
Sand, trace of clay
Sand and gravel, trace of clay
DEPTH BELOW LAND SURFACE, IN FEET
0
5
10
15
20
25
30
35
Bundle of tubes from 7 sampling ports
Land surface
Sand
0.5 ft
8½-inch auger hole
Bentonite grout
2-inch I.D. steel pipe
Static water level
15.8 ft
Sand
17.4 ft Bottom of augered hole
20.50 ft
Screened zone
25.54 ft

Figure 3. Natural gamma-ray log of test hole for sampler 7-8 and diagram of sampler 7-8 installation. (Split-spoon cores were collected from a corehole 10.3 feet from the sampler location.)

The multiport sampler with the attached FEP sample tubing and carbon-steel riser pipe was lowered into the augers and then hammered to its final depth with a safety hammer by using a rope and cathead. As the multiport sampler was driven, additional lengths of riser pipe were pulled over the 33-ft-long FEP sample tubes and were threaded onto the riser pipe within the hollow-stem auger. While the sampler was being driven, deionized water was pumped down the FEP sample tubes to flush the screen sections and to keep aquifer sediments from clogging the screen openings. When the final depth was reached, 1 to 2 ft of fine sand was added to the annular space; then a bentonite slurry was added to the annular space as the auger flights were withdrawn from the hole. The bentonite extends to about 0.5 ft below land surface. Sand was added from the top of the bentonite slurry to land surface. The installation was completed by threading a recorder housing onto the riser pipe within which the coiled bundle of FEP sampling tubes was stored.

Sampling

Water samples were obtained by using two peristaltic pumps in parallel, each having one motor driving seven pump heads. Each pump head had 2 ft of Norprene[2] peristaltic pump tubing. All seven pump heads turned at the same number of revolutions per minute (RPM). At the maximum RPM, the maximum pumping rate for each pump head was 280 mL/min (milliliters per minute) and the maximum vacuum was 24 in. of mercury (Cole-Parmer, 1990). Water was pumped from each sample zone simultaneously at rates ranging from 275 to 360 mL/min for sampler 7-8 and from 265 to 400 mL/min for sampler 5-6. Water from each sampler was purged for 30 minutes before samples were collected in sets of five 40 mL (milliliter) volatile-organic-compound (VOC) vials. The samples were put in a cooler with ice, transported to the USGS New Jersey District laboratory, and stored in a refrigerator at 4 °C (degrees Celsius) until they were analyzed. All 14 samples were analyzed within 7 days from the day the samples were collected.

Laboratory Analysis

The VOC samples were analyzed at the USGS New Jersey District laboratory by using a modification of U.S. Environmental Protection Agency method 502.2 (Slator and Ho, 1989). The modifications include the use of a trap containing Carbopack B and Carbosieve S-III and the use of a Supelco Vocol glass capillary column with the following dimensions: 0.75 millimeter ID, 60 meters long, and a 2.0-micrometer-thick stationary phase. The oven temperature program was from 5 °C to 170 °C at a rate of 4 °C per minute, then from 170 °C to 230 °C at a rate of 20 °C per minute. The final oven temperature of 230 °C was held for 3 minutes. A 10.0-electron-volt photoionization lamp was used in the photoionization detector. The following aromatic compounds were quantified: benzene; toluene; ethyl benzene; meta-xylene plus para-xylene; ortho-xylene; isopropyl benzene; n-propyl benzene; 1,3,5 trimethyl benzene; tert-butyl benzene; 1,2,4 trimethyl benzene; sec-butyl benzene; n-butyl benzene; and napthalene.

VERTICAL CONCENTRATION GRADIENTS OF VOLATILE AROMATIC HYDROCARBONS

Concentrations of selected aromatic compounds as a function of depth are shown in figures 4 and 5 for samplers 5-6 and 7-8, respectively. Although the two samplers are only 55 ft apart laterally, concentrations of the aromatic compounds differed by a factor of approximately 1,000. At sampler 5-6, the volatile aromatic hydrocarbon concentrations ranged from 42.3 mg/L (milligrams per liter) for toluene to 0.04 mg/L for isopropyl benzene; at sampler 7-8, they ranged from 266 µg/L (micrograms per liter) for benzene to 0.6 µg/L for 1,3,5 trimethyl benzene. For all compounds quantitated at both multiport sampler locations, concentrations were lowest at the top and bottom of the sampling interval and were highest near the middle of the interval, as shown in figures 4 and 5. In sampler 5-6, all compounds showed a similar concentration variation with depth (fig. 4), whereas, at sampler 7-8, the variation in the concentration of benzene with depth (fig. 5) differed from that of the other compounds.

Variations in pumping rate with depth or sample port were observed during sampling (figs. 4 and 5). All peristaltic-pump heads turned at the same rate to produce the same pumping pressure at each sample port. The frictional head losses within the multiport sampler were equal for each port, except for the differences in frictional resistance to flow caused by the different tubing lengths to each port. The maximum change in head loss among ports caused by the difference in tubing length was calculated to be equivalent to 2.2 in. of water. The total head loss caused by friction and form resistance within the multiport sampler at a sampling rate of 250 mL/min was calculated to be equivalent to 5.8 in. of water. These calculations are based on the piping-loss equations shown in Foust and others (1980). These losses caused by friction and form resistance were small relative to the total head required to lift water from the water table to land surface (approximately 15 ft; see figs. 2 and 3). Therefore, the observed variations in pumping rates probably were caused by corresponding variations in aquifer hydraulic conductivity over the screened length of each multiport sampler.

The vertical variations in concentrations of aromatic compounds in the plume, shown in figures 4 and 5, indicate that a conventional well screen would have to be less than 3 ft long to be smaller than the thickness of the plume at both multiport-sampler locations. The use of a conventional well screen 5 ft long would result in underestimates of the maximum concentrations in the plume. For example, the flow-rate-weighted average concentration of benzene, shown in table 1, was 42.2 percent and 28.2 percent of the maximum observed concentration for samplers 5-6 and 7-8, respectively. The flow-rate-weighted average concentration of orthoxylene was 60 percent of the maximum observed concentration for sampler 5-6.

Differences in hydraulic conductivity of the formation as a function of depth over the screened interval cause

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[2] Use of trade, firm, or brand names in this paper is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

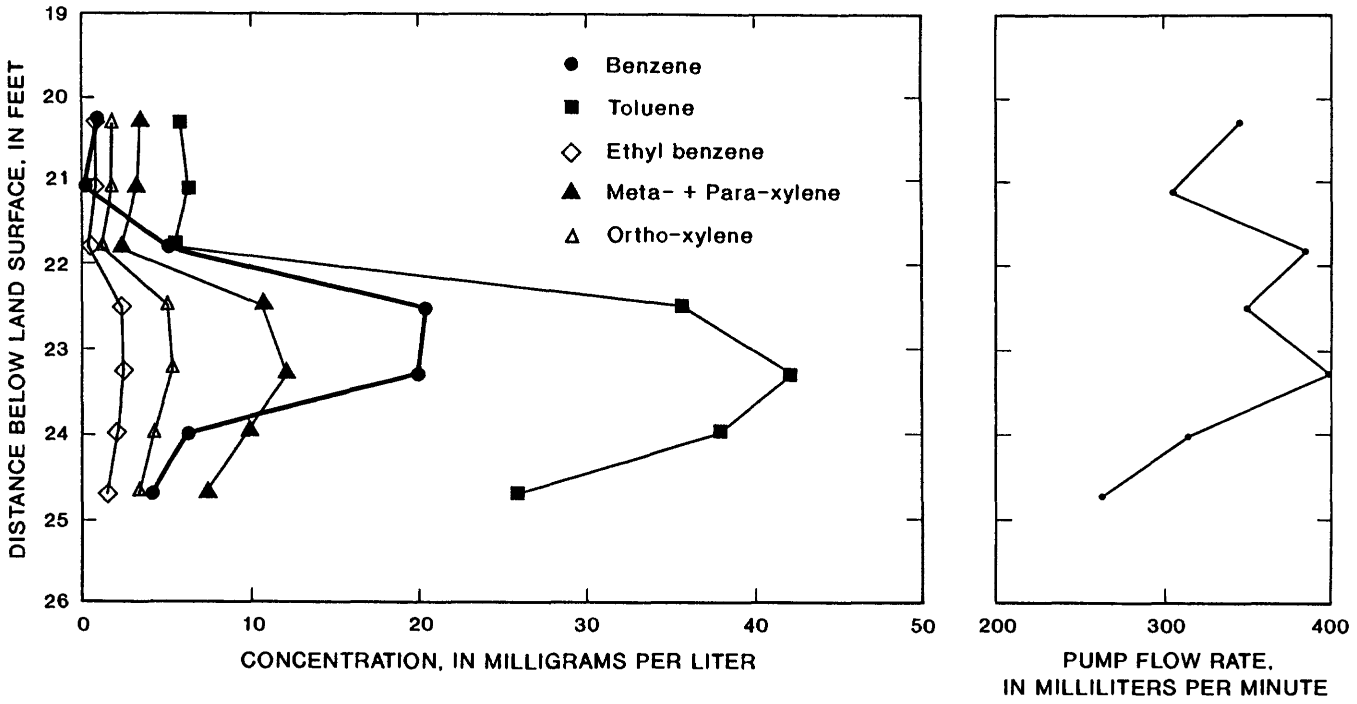

Figure 4. Variation in concentrations of volatile aromatic hydrocarbons and pump flow rate with depth at multiport sampler 5-6.

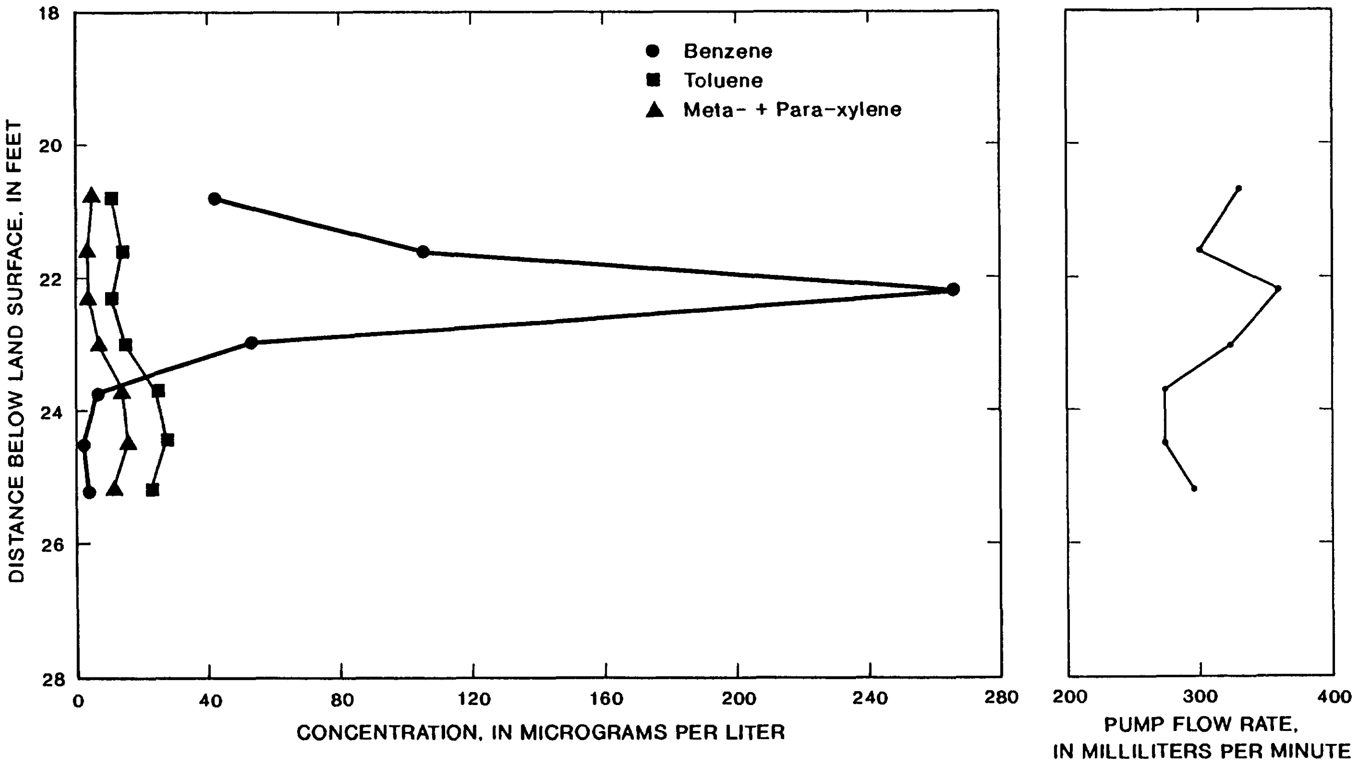

Figure 5. Variation in concentrations of volatile aromatic hydrocarbons and pump flow rate with depth at multiport sampler 7-8.

Table 1. *Maximum, flow-rate-weighted average, and mean concentrations of volatile aromatic hydrocarbons determined for a 5-foot screen*

[mg/L, milligrams per liter; µg/L, micrograms per liter]

	Sampler 5-6			Sampler 7-8		
Volatile aromatic compound	Maximum concentration (mg/L)	Flow-rate-weighted-average concentration[1] (mg/L)	Mean concentration[2] (mg/L)	Maximum concentration (µg/L)	Flow-rate-weighted-average concentration[1] (µg/L)	Mean concentration[2] (µg/L)
Benzene	20.6	8.7	8.2	266.0	74.9	68.5
Toluene	42.3	22.8	22.7	27.3	17.4	17.9
Ethyl benzene	2.5	1.5	1.5	3.2	1.8	1.9
Meta-xylene and para-xylene	12.1	7.08	7.03	16.3	8.6	8.9
Ortho-xylene	5.3	3.2	3.2	7.1	5.1	5.5

[1] Flow-rate-weighted average concentration

$$= \frac{\sum_{i=1}^{7} \text{concentration}_i \times \text{flow rate}_i}{\sum_{i=1}^{7} \text{flow rate}_i}$$

[2] Mean concentration

$$= \frac{\sum_{i=1}^{7} \text{concentration}_i}{7}$$

variations in the rate at which water flows into the well (see figs. 4 and 5). The flow-rate-weighted average concentration for the multiport samplers approximates the effect of these variations on analyte concentrations in a conventional well by biasing the analyte concentrations in the water collected with the multiport sampler toward the concentrations in the zones having the highest hydraulic conductivity. The flow-rate-weighted average concentration commonly is different from the mean concentration. As shown in table 1, the mean concentration of benzene for sampler 5-6 was 8.2 mg/L, whereas the flow-rate weighted average concentration was 8.7 mg/L. The difference between the flow-rate-weighted average and the mean can be even greater if the variation in hydraulic conductivity in the screened zone is greater.

SUMMARY AND CONCLUSIONS

A multiport sampler was designed to investigate the ability of conventional observation wells to yield representative samples of ground water where contaminant concentrations may vary with both depth and time during well purging and sampling. The sampler was installed without a gravel pack and simulates a conventional wire-wound screen but, unlike the conventional screen, allows samples to be collected from seven discrete depths within the screened zone. The sample-analysis results show that where contaminant concentrations vary with depth, a conventional well can yield samples with concentrations much lower than the maximum concentration. For example, at sampler 7-8 the flow-rate-weighted average concentration of benzene was 28 percent of the maximum concentration of benzene. At sampler 5-6, this percentage was 42 percent for benzene and 60 percent for ortho-xylene, showing that this difference can vary with site and for different contaminants at the same site. The collection of representative samples from conventional observation wells is difficult because a proportionally greater amount of sample water is derived from zones of high hydraulic conductivity than from zones of lower hydraulic conductivity. The results of this study indicate that the length of the screen (physical scale) at which samples are collected affects the apparent water quality when sampling ground water for trace concentrations of organic compounds.

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USE OF MATHEMATICAL PROGRAMMING COUPLED WITH A TRANSPORT MODEL TO OPTIMIZE THE DESIGN OF VAPOR-EXTRACTION SYSTEMS

By Claire Welty[1], Arthur L. Baehr[2], Craig J. Joss[1], and Jonathan J. A. Dillow[1]

ABSTRACT

An approach for simulating optimal design of vapor-extraction systems is presented. A three-dimensional, steady-state, air-flow model coupled with an optimization algorithm is being developed to determine optimal pumping rates and placement of venting wells for withdrawing volatile contaminants from soil. Two problems will be solved and results will be compared using the coupled air-flow/optimization code: a flow-maximization problem and a cost-minimization problem. Problem constraints include maximum or minimum total flow rate (and corresponding vacuum) at each well and budgetary constraints.

A second component of this work is development of a three-dimensional, transient, compositional model to simulate subsurface hydrocarbon-vapor transport and microbial degradation. This numerical model will be linked to an optimization algorithm to determine a schedule of air withdrawal/injection rates at the well locations previously found using the air-flow/optimization code. The objective will be to minimize cleanup costs during a specified time period, subject to budgetary constraints, and a target subsurface distribution of contaminants in the vapor and(or) the soil. Finally, a new field method for determining air-phase permeabilities is discussed.

INTRODUCTION

Soil venting is used as a remediation technique to reduce the mass of hydrocarbons in soils to an environmentally acceptable level in a cost-effective manner. Although this method has been implemented widely (Texas Research Institute, Inc., 1980), design of such systems remains more an art based on experience rather than the product of rigorous analysis (Johnson and others, 1990), in part because three-dimensional mathematical models to simulate the air-flow process previously have been unavailable. Drexel University, in cooperation with the U.S. Geological Survey (USGS) and the American Petroleum Institute, has undertaken a project to fill this gap in available technology. The goal is to develop a three-dimensional, compositional transport model to simulate hydrocarbon transport and microbial degradation under general soil-venting scenarios, and to couple this model with an optimization algorithm to determine optimal venting-well placement and air-pumping rates under imposed cost and time limitations and desired contaminant levels. The results of this project will aid in the design of venting-well systems by enabling the user to predict soil-venting performance under various venting configurations and physical and regulatory conditions. This paper discusses the general approach taken by the authors in developing the coupled simulation/optimization model.

OPTIMIZATION OF VAPOR-EXTRACTION SYSTEM DESIGN

Optimization Formulation

Optimal location and pumping rates of venting wells screened in the unsaturated zone must be selected. The design question can be formulated as an optimization problem in which the objective function is to minimize total costs of hydrocarbon venting subject to the constraints of the system. The decision variables are well locations and withdrawal/injection rates. In its fully stated form, this problem is a mixed-integer, nonlinear optimization problem. In order to reduce computational complexity and to take advantage of uncoupled numerical solutions to the air-flow equation and the hydrocarbon-transport equation, the optimization problem is divided into two parts.

In the first part of the problem, optimization linkage is used solely with the air-flow model. The objective is to either maximize total flow rate over a subdomain of the modeled site or minimize total costs of pumping, subject to a number of constraints. For both objectives, the three-dimensional permeability field acts as a constraint through the flow equation, with flow induced by withdrawal only or by a combination of withdrawal and injection at different wells. Maximum permissible flow rates (and corresponding vacuums) at each well are optional constraints. For the flow-maximization problem, a maximum total flow rate also must be specified. The flow maximization problem can be solved by coupling the air-flow model with a linear-programming algorithm, inasmuch as the objective function and constraints are all linear functions of flow rates. The locations at which optimal withdrawal/injection rates are found to be zero or very small can be considered to be poor candidates for well installation.

For the cost-minimization problem, a total minimum flow rate must be specified as a constraint; a total budget for the project also can be specified as an optional constraining condition. Variable costs of pumping (in dollars per kilowatt-hour of electricity used) and fixed costs (well-installation costs, pump-purchase costs, monthly electric rates) can be incorporated as cost coefficients of the decision variables in the objective function and in the budget constraint. If fixed costs are included in this problem, the use of a mixed-integer/linear-programming formulation is required, where an integer (binary) decision variable indicates whether or not withdrawal or injection occurs at a particular location, and the flow rates can take on any continuous

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value, as in the flow-maximization problem. All constraints are linear functions of the two decision variables. Use of the integer decision variable requires the use of a mixed-integer/linear-programming algorithm coupled with the air-flow model. A number of problems that can be solved by using an optimization algorithm coupled with the air-flow algorithm are summarized in figure 1.

Once the optimal-well-location decision has been made on the basis of one of the above approaches, the next design question is the length of time a pump must operate at each well to reduce vapor-contaminant concentrations to desired levels at the pumping locations. An additional level of complexity can be introduced by employing fewer pumps than installed wells, where the pumps can be moved from well to well. A pump also can be reused at a well at a later time if the vapor concentrations begin to exceed target contaminant levels. Optimal pumping schemes also can be explored to determine whether more vapor mass is removed per unit of flow rate by continuous or pulsed pumping.

This pump-scheduling problem is solved by coupling an optimization algorithm with a transient vapor-transport model. This problem can be formulated as a cost-minimization problem that is subject to regulatory, budgetary, and flow constraints. It is a nonlinear problem because pumping rates and vapor concentrations are unknown in the optimization problem. A similar problem for two-dimensional, transient contaminant transport in ground water has been solved by Gorelick and others (1984). If fixed costs are included, and(or) the problem is formulated to allow fewer pumps than wells, the problem becomes a mixed-integer/nonlinear problem, which is very difficult to solve and for which no widely available, documented solution algorithms exist.

In order to solve either problem, a number of factors are specified as problem inputs and constraints. First, only nodes at which wells have been installed are candidates for pumping. Second, the three-dimensional permeability field acts as a constraint through the flow equation. Third, a total time during which the remediation must be achieved and the length of uniform pumping periods are specified. Fourth, a target criterion for contaminant distribution in the vapor or soil is chosen. Fifth, if the nonlinear formulation is to be used with continuous decision variables (that is, flow rates), then the number of pumps available must equal the number of wells, and fixed costs (monthly electric charges) cannot be included. If the integer/nonlinear problem is solved, the number of pumps can be less than the number of well locations, and fixed costs can be included in the objective function. Variable costs include the costs of activated-carbon treatment of the vapors, sampling, and kilowatt-hour charges. If a budget constraint is included, the total cost of well installation (found by using the air-flow/optimization model) and the total cost of the pumps can be subtracted from the total budget. Finally, maximum permissible pumping rates can be specified at each well. A total minimum flow rate need not be specified to force the total costs (objective function) to be greater than zero; the target contaminant levels serve instead to force dollars to be spent. A number of problems that can be solved by coupling the optimization algorithm with the vapor-transport model are summarized in figure 2.

Vapor-Transport Model

The vapor-transport model is being developed in two stages. First, a module is being developed to solve for the three-dimensional movement of bulk air under venting conditions by adapting the USGS flow code, MODFLOW (McDonald and Harbaugh, 1984), to conditions of steady-state air-flow, where the square of the air-phase pressure appears as the dependent variable in place of hydraulic head. Thus, the definition of the induced flow field is uncoupled from vapor transport. The theoretical basis for this approach is described in Baehr and Hult, 1991.

Flow vectors computed from the air-flow module are then available to the vapor-transport model, which consists of a conservation-of-mass equation for each hydrocarbon constituent as well as for the gases of interest, including electron acceptors (for example, oxygen) and other gases (for example, carbon dioxide, methane). These constituent-specific transport equations are coupled by means of phase-partitioning constitutive relations and the submodel defining microbial degradation.

This approach is being used for the following reasons. First, under conditions of induced flow, the effect on flow of air-density differences caused by variations in vapor composition is small compared to the flow component resulting from the pressure gradient caused by venting. Uncoupling also is recommended because of the discrepancy between the cost and difficulty of collecting the physical data (that is, pressures, characterization of unsaturated-zone strata) required to calibrate an air-flow model and those needed to support a transport model (that is, sophisticated organic-compound-analysis equipment and highly trained field personnel). The "weak link" in prediction of the vapor-contaminant distribution for routine applications of the venting technique will be the determination of the spatial and temporal distribution of chemical constituents. Because the practitioner may consider making design decisions on the basis of an accurate flow-field estimate with a crude estimate of contaminant distribution, the numerical methods and nodal spacings required for each module ideally should be determined independently. Interpolation techniques to make the scales of the individual modules compatible with each other are being developed.

The numerical method employed to solve the transport-model equations is being developed with a sensitivity to data availability. A finite-element- or finite-difference-based technique is anticipated. The appropriateness of neglecting dispersive transport, an approximation that would afford great numerical simplification, is being examined theoretically.

A field technique for determining air-phase permeability in the unsaturated zone is being developed to provide a cost-effective, practical method of obtaining reliable field data for use in air-phase transport models. A particular application of the technique uses vapor probes positioned strategically within discrete subsurface strata. The localized effects of the air withdrawal used in the test permit a measurement of permeability in the selected strata. The apparatus used in the field studies includes a pneumatic pump, a length of stainless-steel tubing, a flowmeter, a water manometer, a thermometer, and a barometer. The end of the

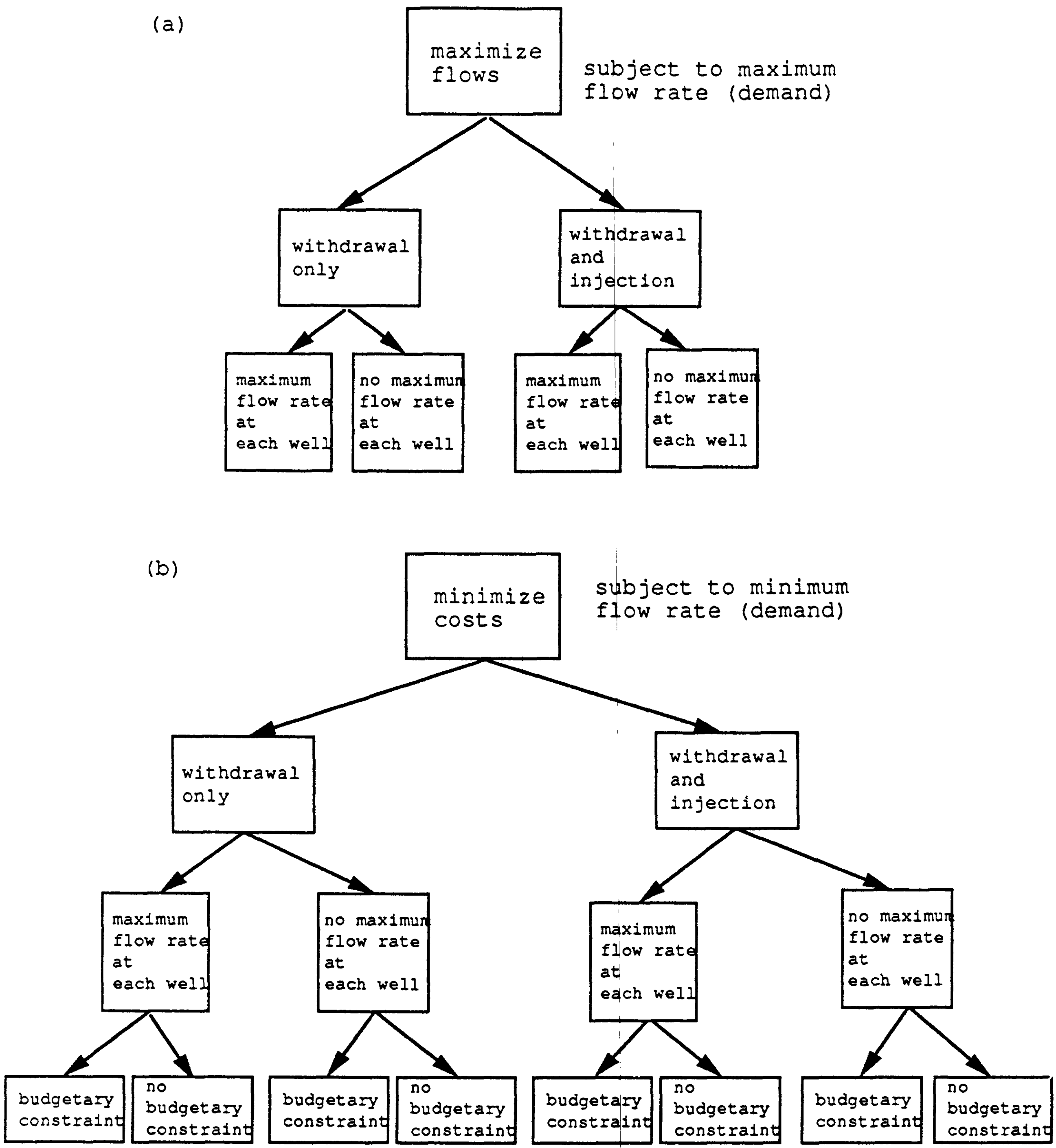
(a)
maximize flows
subject to maximum flow rate (demand)
withdrawal only
withdrawal and injection
maximum flow rate at each well
no maximum flow rate at each well
maximum flow rate at each well
no maximum flow rate at each well
(b)
minimize costs
subject to minimum flow rate (demand)
withdrawal only
withdrawal and injection
maximum flow rate at each well
no maximum flow rate at each well
maximum flow rate at each well
no maximum flow rate at each well
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Figure 1. Problems to be solved by using an airflow model coupled with a (a) linear or (b) mixed-integer/linear-programming algorithm.

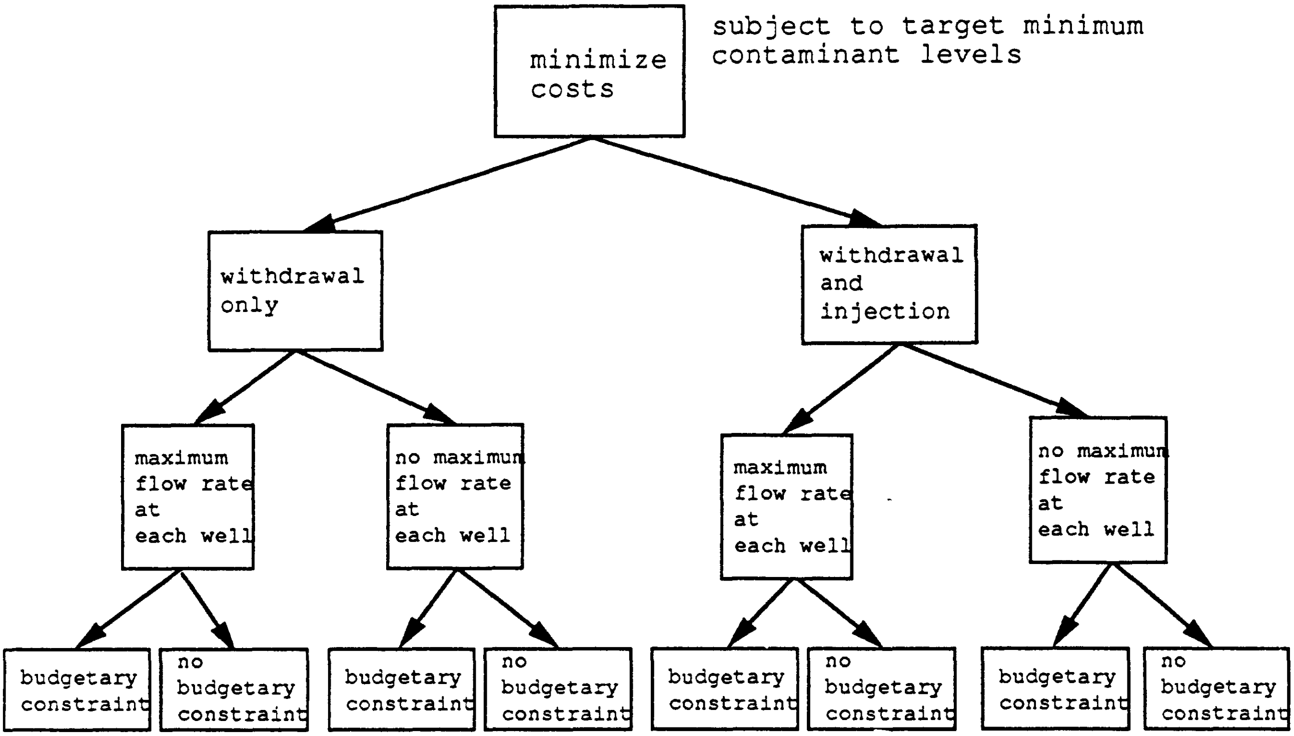
minimize costs
subject to target minimum contaminant levels
withdrawal only
withdrawal and injection
maximum flow rate at each well
no maximum flow rate at each well
maximum flow rate at each well
no maximum flow rate at each well
budgetary constraint
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Figure 2. Problems to be solved by using a vapor transport model coupled with a (a) nonlinear or (b) mixed-integer/nonlinear-programming algorithm. For (a) the number of pumps equals the number of wells and fixed costs are not included. For (b) the number of pumps can be less than the number of wells, and fixed costs can be included in the objective function.

tubing is modified to form a vapor probe by drilling holes over a specified length of screen. The screen is then set in a sand pack located approximately at middepth in a delineated zone. The augered hole is sealed at the top and bottom of the sand pack with a bentonite layer. The test procedure consists of extracting air from the geologic strata at various flow rates and measuring variations in system pressure and air-flow rates. Surface and subsurface temperatures and barometric pressures also are recorded. With this information, the air-permeability of a selected region of the vadose zone can be determined by calibration of the analytical air-flow model presented by Baehr and Hult (1991).

SUMMARY

Three-dimensional air-flow and vapor-transport models are being developed by researchers at Drexel University in cooperation with the U.S. Geological Survey and the American Petroleum Institute. These models will be coupled with mathematical optimization algorithms to design optimal vapor-extraction systems for removal of subsurface vapor contamination. The information to be obtained with this approach includes optimal number and placement of venting wells, pumping rates, and a pumping schedule for site cleanup at minimum cost. The use of three-dimensional models will allow accurate assessment of the effects of vertical permeability distribution on the flow field. A field technique for determining air-phase permeabilities has been developed to obtain input data needed for the air-flow model.

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GAS-CHROMATOGRAPHIC METHODS FOR DETERMINING THE COMPOSITION OF THE VAPOR PHASE IN GASOLINE-CONTAMINATED SOILS

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ABSTRACT

A gas chromatograph with flame-ionization and thermal-conductivity detectors is being used to monitor concentrations of hydrocarbons and inorganic gases in unsaturated-zone soil-gas samples. The gas chromatograph is located at the site of an underground gasoline spill in Galloway Township, New Jersey. Inorganic gases are detected by thermal-conductivity-detector analysis and quantified by use of linear regression standard curves. Hydrocarbons are detected by using flame-ionizationdetector analysis, and 16 specific hydrocarbons are identified by their retention times and are quantified by using linear regression analysis. A method of carbon number analysis was developed to facilitate semiquantitative evaluation of flame-ionization chromatograms that contained unidentified peaks. Carbon number analysis involves partitioning chromatograms into retention time increments assuming that each increment contains hydrocarbons having the same number of carbon atoms.

INTRODUCTION

Spills of organic liquids, such as gasoline and industrial solvents, pose a threat to ground-water quality. Remedial action commonly is limited to removing the organics by pumping and treating the ground-water; however, a significant part of the contaminant usually remains in the unsaturated zone, providing a long-term source of ground-water contamination (Baehr, 1987). Because gasoline-range hydrocarbons are highly volatile, they can be transported in the vapor phase. Therefore, monitoring the organic composition of soil-gases is an important component of any unsaturated zone study or remediation process where volatile hydrocarbons are present. For example, monitoring the composition of soil gases in microbially active, hydrocarbon-contaminated areas in the unsaturated zone allows estimation of *in-situ* biodegradation rates.

As part of a study being conducted by the U.S. Geological Survey at a gasoline spill site in Galloway Township, N.J. a soil-gas sampling network was installed and a field laboratory trailer was set up at the site. A gas chromatograph (GC) was configured to analyze soil-gas samples for gasoline hydrocarbons and inorganic gases, such as oxygen (O_2), nitrogen (N_2), nitrous oxide (N_2O), carbon monoxide (CO), and carbon dioxide (CO_2). This instrument was selected over other analytical options because of its versatility; it can be used to monitor all significant organic and inorganic components of unsaturated-zone gases. Previous work at another hydrocarbon-contaminated site showed that gas samples containing volatile organic compounds have limited stability through time (Kammer and Smith, 1989), therefore, the GC is located onsite to minimize holding times.

GC data commonly are used to identify and quantify components of samples. Generally, standards are prepared from known amounts of substances of interest, the standards are injected into the chromatograph, and GC retention times are determined for these substances. The magnitude of GC-detector response is determined for known concentrations of each analyte. GC peaks are then identified by retention time, and the substances are quantified by the magnitude of the GC detector response from chromatograms of "real" samples. This approach was used to identify and quantify concentrations of 16 gasoline hydrocarbons and 4 inorganic gases in soil-gas samples at the Galloway Township site.

Complex chromatograms with numerous unidentified peaks, such as those for hydrocarbon analysis from the Galloway Township site, must be evaluated by more general procedures, because identification and quantification of each individual peak is impractical or impossible. Although 16 specific hydrocarbons were identified and quantified, many other peaks remained unidentified. Therefore, a method of chromatogram evaluation was developed that does not require identification of specific peaks. The method involves dividing chromatograms into retention time increments, each containing peaks of compounds having the same number of carbon atoms (carbon number). The method is based on relations between carbon number and boiling point, and between boiling point and GC retention time, and is described in detail in this paper.

This paper describes the GC analysis used to monitor the vapor-phase composition of the unsaturated zone in an area contaminated by an underground gasoline spill. The GC and data processing system are described. Methods for identifying and quantifying selected hydrocarbons and inorganic gases are presented, and a technique for evaluating complex chromatograms containing unidentified peaks is described in detail. This chromatogram evaluation technique is demonstrated by using an example chromatogram.

DESCRIPTION OF GAS-CHROMATOGRAPHIC METHODS

Chromatographic and Data-Processing System

A Tracor 540[2] GC with a thermal-conductivity detector (TCD) and a flame-ionization detector (FID) is being used for this field study. Figure 1 shows system configuration; analytical conditions are shown in table 1.

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[1] U.S. Geological Survey, West Trenton, N.J.

[2] Use of brand, firm, or trade names in this paper is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

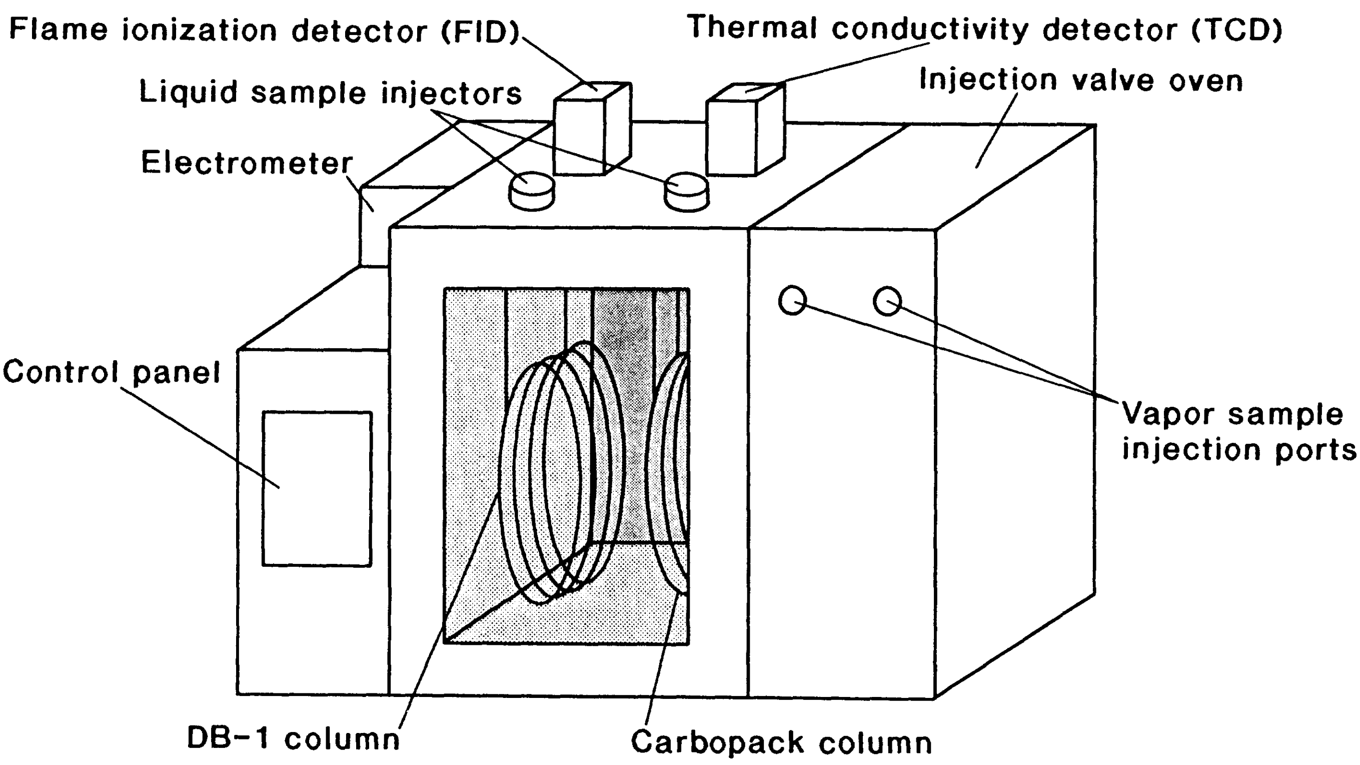

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Figure 1. Configuration of the gas chromatograph.

Table 1. *Analytical conditions*

[°C, degrees Celsius; mL, milliliter; min, minute; UHP, ultra-high purity; m, meters; mm, millimeters; µL, microliters; He, helium; mL/min, milliliters per minute; °C/min, degrees Celsius per minute; ID, internal diameter]

Instrument: Tracor 540 gas chromatograph
Sample injection: 2 splitless injectors, each with a heated gas sample injection system
Heat zones:
  Detectors: 105 °C
  Injectors: 250 °C
  Flow controllers: 40 °C
  Injection valve oven: 80 °C
Hydrocarbon analysis
  Sample size: 2 mL vapor samples
  Carrier gas: 5.0 mL/min UHP-grade He
  Column: 30m x 0.53mm ID DB-1, 3.0 ξm film
  Temperature program: 35 °C for 3 min, raise at 2.5 °C/min to 110 °C.
  Detector: flame ionization (FID)
    Make-up gas: 60 mL/min UHP-grade He
    Flame: 300 mL/min dry-grade air, 30 mL/min UHP-grade He
    Electrometer attenuation: input = 1, output = 5
Inorganic-gas analysis
  Sample size: 5 mL vapor samples
  Carrier gas: 40 mL/min UHP-grade He for column and reference stream
  Column: 3.3m x 6.35mm ID stainless steel, 100 percent Carbopack
  Temperature program: 35 °C for 4 min, raise at 35 °C/min to 200 °C, hold for 2.1 min
  Detector: thermal conductivity (TCD)
    Sensitivity: 1
    Output attenuation: 200
Data collection, processing, and storage system
  Computer: IBM PS/2, Model 60
  Data system: PE-Nelson 2100 PC-Integrator

The TCD uses a 3.3 meter-long stainless-steel Carbopack column for analysis of inorganic gases and methane. The FID is used with a 30 meter-long DB-1 capillary column for analysis of hydrocarbons.

In order to ensure uniform sample size, vapor-sample-injection valves are used to accurately meter gas samples into the chromatograph. Each GC column is equipped with its own injection valve, fitted with a sample loop. The sample loop volume determines the sample size injected into the GC. Optimum peak size and separation were attained by using a 5-mL (milliliter) loop with the Carbopack column for TCD analysis and a 2-mL sample loop with the DB-1 column for FID analysis. Lower minimum detection limits could be achieved by using a loop larger than 5 mL for TCD analysis of the inorganic gases, but the close proximity of oxygen and nitrogen peaks resulted in incomplete separation of these two species; therefore, increasing the loop size beyond 5 mL would have caused unacceptable compromises in quantitative precision. The two vapor-sample-injection valves reside in an oven adjacent to the GC column oven, and are maintained at 80 °C (degrees Celsius).

A PC Integrator Model 2100 chromatographic data system is being used for data collection, processing, and storage. This software is run on an IBM PS-2 Model 60 computer. Inorganic gas and hydrocarbon data are processed separately in this two-channel system. Analog signals from the chromatograph are converted to digital data points by an analog-to-digital interface. Each digital data point represents a microvolt reading from a detector at a specific time. The digital data points are reassembled into a chromatogram by the PE-Nelson software. Data-point sampling frequency can be varied, and the optimum sampling rate gives an accurate reproduction of the chromatogram while avoiding excessive use of computer disk space.

Compound Identification and Quantification

Oxygen, nitrogen, and carbon dioxide were separated and quantified by TCD analysis using the Carbopack column. Linear regression calibration curves were prepared by using commercially available gas standards. Calibration standards between 330 and 990,000 parts per million were used. Precision of quantification, as determined by replicate analysis, is presented in table 2.

Table 2. *Retention times and quality-assurance data for hydrocarbons and inorganic gases*

[FID, flame ionization detector; RT, retention time; LOD, limit of detection; LOQ, limit of quantification; min, minutes; μg/L, micrograms per liter; TCD, thermal conductivity detector; ppm, parts per million; n, number of replicates; --, no data]

Compound (FID)	RT (min)	Precision[1]	LOD[2] (μg/L)	LOQ[3] (μg/L)
Pentane	2.03	0.4	0.03	0.27
Chloropropane[4]	2.43	--	--	--
1-Hexene	3.27	4.3	.02	.27
Hexane	3.48	3.4	.03	.27
Benzene	4.87	1.8	.03	.27
Cyclohexene	5.78	6.0	.03	.27
Heptane	6.97	1.8	.03	.27
Chloropentane[4]	9.16	--	--	--
Toluene	9.93	.8	.02	.27
Octane	12.87	1.0	.03	.27
Ethylbenzene	15.91	1.2	.02	.27
m- and p-Xylene	16.48	2.1	.02	.27
o- Xylene	17.93	10.9	.02	.27
Nonane	19.48	1.1	.03	.27
Propylbenzene	22.02	5.1	.02	.27
Chloroheptane[4]	22.38	--	--	--
1,2,4-Trimethylbenzene	24.59	13.9	.02	.27
Decane	25.97	2.1	.03	.27
1,2-Diethylbenzene	28.82	24.7	.02	.27

Compound (TCD)	RT (min)	Precision[1]	LOD[2] (ppm)	LOQ[3] (ppm)
Oxygen	2.87	4.0	40,000	40,000
Nitrogen	3.00	0.4	--	--
Methane	7.70	0.3	200	667
Carbon dioxide	9.50	2.1	200	667

[1] Percent coefficients of variation for replicate analysis: n = 5 (FID); n = 7 (carbon dioxide); n = 9 (other TCD compounds).

[2] Limit of detection.

[3] Limit of quantification.

[4] Retention-time reference standards.

Sixteen hydrocarbon compounds (HC) were identified in the unsaturated zone samples by matching GC peak retention times with retention times of standards; 1-chloro-n-propane, 1-chloro-n-pentane, and 1-chloro-n-heptane were used as retention time reference peaks to minimize peak misidentifications caused by slight deviations in retention times. Vapor-phase HC standards were prepared by injecting known amounts of pure compounds into helium-filled static-dilution-bulbs of known volume (approximately 2 liters). Calibration standard concentrations of 0.27 to 72.7 micrograms per liter were used. Linear regression standard curves were used to quantify the 16 compounds. Precision data are presented in table 2.

A method developed by Long and Winefordner (1983) was used to determine limits of detection and limits of quantification for the inorganic gases and hydrocarbons. Generally, a signal significantly larger than background noise indicates the presence of an analyte. Limits of detection were determined from background noise levels by using the following steps:

1. Background noise levels for FID and TCD analysis were determined automatically by using PE Nelson 2700 Turbochrome software.
2. Minimum peak areas were designated. Peaks smaller than these minimum values were considered background noise and were disregarded.
3. Limits of detection were calculated from the minimum peak areas for each species monitored.
4. Limits of quantification were determined from the definition of Taylor (1987), as (10/3) x limit of detection. When this number was smaller than the concentration of the most dilute standard used for standard curve prepatation, the most dilute standard was considered the limit of quantification.

Limits of detection and quantification for the 5 inorganic gases and 16 hydrocarbons are listed in table 2.

Flame Ionization Detector Chromatogram Evaluation By Carbon-Number Analysis

Because gasoline is a mixture of hundreds of different hydrocarbons, identification of all compounds on the FID chromatograms is impossible; however, because much information is contained in these complex chromatograms, a method of evaluating them was developed that does not require specific peak identification. In this approach chromatograms are divided into retention time increments. The peaks in each increment represent compounds, all of which are assumed to have the same carbon number (C-5, C-6, C-7, C-8, C-9, or C-10). A sample can then be described semiquantitatively in terms of the number of compounds of each carbon number, total mass of each carbon number, or percent of mass represented by each carbon number.

This section describes the procedure used to locate retention times marking the boundaries between adjacent carbon-number increments. The procedure relies on a mathematical relation between GC retention time and boiling point for gasoline hydrocarbons and on a relation between carbon number and boiling point for gasoline hydrocarbons.

The DB-1 nonpolar capillary column separates gasoline hydrocarbons by boiling point. A log-linear relation between retention time and boiling point can be observed for hydrocarbons chromatographed isothermally (Chemical Rubber Company, 1972). In this study, however, programmed temperature GC was used, so no such relation exists. In order to determine how retention time is related to boiling point in this study, retention times of the 16 hydrocarbons in table 2 were plotted as a function of boiling point, and the following second-order relation was determined by curve fitting:

$$RT = 1.513 - 0.02462(BP) + 0.0009601(BP)^2, \qquad (1)$$

where

RT = compound retention time, and
BP = compound boiling point.

The correlation coefficient for this relation is 0.9994. This relation enables estimation of the GC rention time for any gasoline hydrocarbon compound for which the boiling point is known. Retention times of 167 gasoline-range hydrocarbons were estimated in this manner from published boiling point data (Chemical Rubber Company, 1988).

The relation between carbon number and boiling point is less definitive than that between boiling point and retention time. Boiling points increase predictably in homologous hydrocarbon series as carbon number increases (for example, n-alkanes from methane to decane); however, for a set of hydrocarbons with the same carbon number but varying in degree of saturation and arrangement of the carbon atoms, factors such as branching, double bonds, and aromaticity affect boiling points. Therefore, compounds with a given carbon number have a specific boiling range, and the boiling ranges of different carbon-number sets overlap, as shown in the top part of figure 2. The locations of the lines drawn on the chromatograms to separate the carbon-number sets were determined statistically in order to minimize the number of compounds assigned incorrect carbon numbers, as described below.

The chromatogram illustrated at the bottom of figure 2 is partitioned by carbon number. Lines between carbon-number sets were positioned such that the percentage of compounds of carbon number N falling within the carbon number N+1 region is equal to the percentage of carbon number N+1 compounds falling within the carbon number N region. This chromatogram partitioning was done using the Z distribution of normally distributed data:

$$Z = (X-\mu)/\sigma, \qquad (2)$$

where

Z = standard normal deviate,
X = an individual data point (in this case, a boiling-point),
μ = population mean, and
σ = population standard deviation.

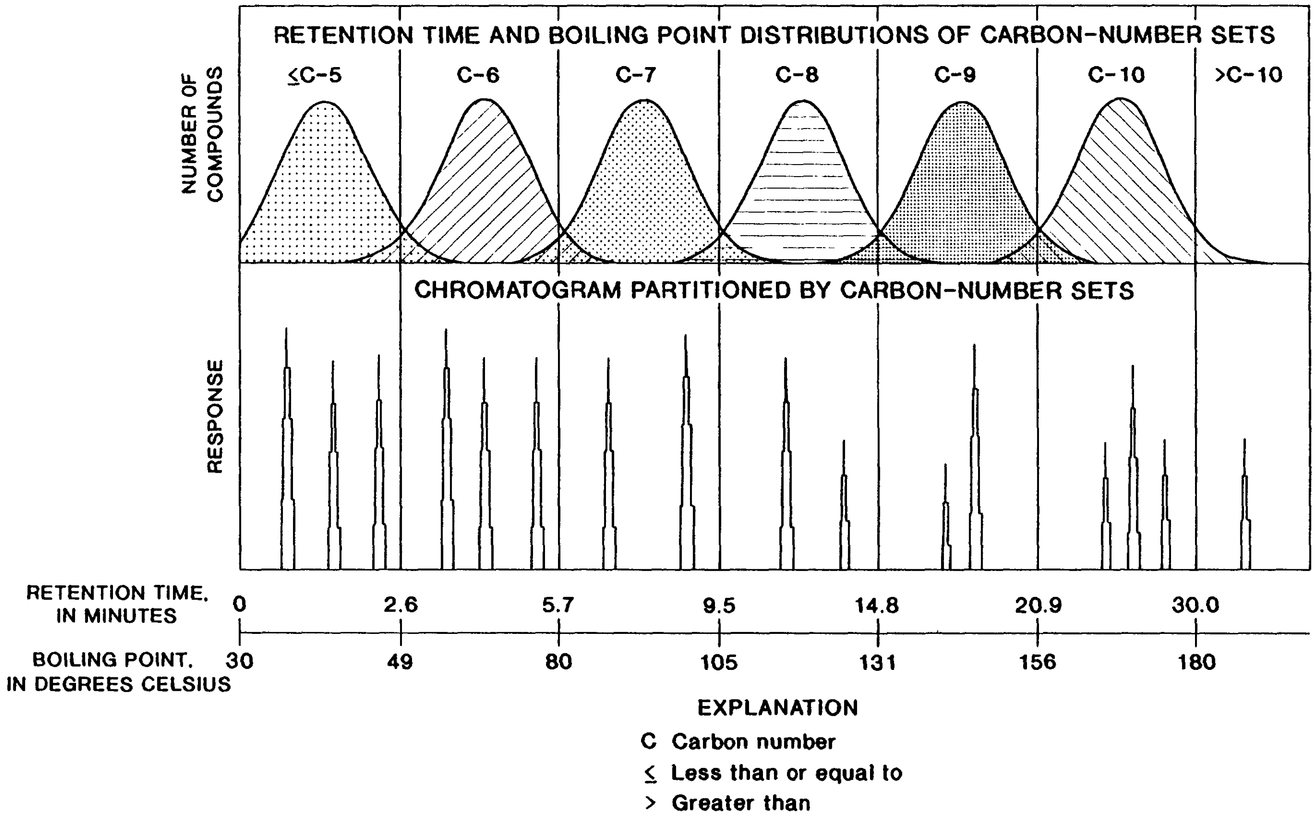

Figure 2. Distribution of carbon number with respect to retention time and boilng point (top); chromatogram partitioned by boiling point (bottom).

At the intersection of regions N and N+1,

$$Z_N = Z_{(N+1)} \tag{3}$$

The boiling point at the border between N and N+1 compounds was calculated by rearranging the Z equations for the N and N+1 regions--

$$BP_{(N,\,N+1)} = [(\mu BP_N)(\sigma BP_{(N+1)}) - (\mu BP_{(N+1)})(\sigma BP_N)]/$$
$$-(\sigma BP_{(N+1)} - \sigma BP_N), \tag{4}$$

where

$BP_{(N,\,N+1)}$ = boiling-point boundary between N and N+1 compound sets,
μBP_N = mean boiling point of hydrocarbons with N carbon atoms, and
σBP_N = standard deviation of boiling points of hydrocarbons with N carbon atoms.

The Z statistic is usually applied to populations, not to samples from populations. In using Z, the assumption was made that the 167 compounds used constitute a sufficiently large part of the gasoline-hydrocarbon population such that the means and standard deviations calculated are accurate estimates of the population statistics. The means and standard deviations of boiling points for each carbon-number set were calculated from published values of boiling points (Chemical Rubber Company, 1988). Retention times for the borders separating carbon-number regions ($RT_{(N,\,N+1)}$) were determined from $BP_{(N,\,N+1)}$ by use of equation 1.

As a result of the significant overlap between adjacent carbon-number distributions, an unknown peak falling within a particular carbon-number region actually may have one more or one less carbon atom than it is assumed to have. Of 167 compounds evaluated, 131 fell into the correct carbon-number segment (78.4 percent), 16 appeared in the next lower segment (9.6 percent) and 20 appeared in the next higher segment (12.0 percent). The percentage of overlap between carbon-number sets is shown in table 3. Accuracy

Table 3. *Carbon-number-analysis of FID chromatograms*

[RT, retention time; BP, boiling point; min, minutes; 'C, degrees Celsius; FID, flame ionization detector; ≤, less than or equal to; ≥, greater than or equal to; --, no data]

	Carbon number[1]					
	≤5	6	7	8	9	≥10
Compounds[2]	9	18	22	41	48	29
Lower retention-time limit[3]	0	2.97	5.64	9.60	14.88	20.91
Upper retention time limit	2.97	5.64	9.60	14.88	20.91	--
Lower boiling-point (°C) limit[4]	--	53.9	79.6	105.5	131.5	155.6
Upper boiling-point (°C) limit	53.9	79.6	105.5	131.5	155.6	--
Percent below range[5]	--	5.82	13.14	8.38	20.90	10.75
Percent within range	94.18	81.04	78.48	70.72	68.35	89.25
Percent above range	5.82	13.14	8.38	20.90	10.75	--

Boundary standards[6]

Boundary	Compound	RT (min)	BP(°C)
C-5/C-6	Cyclopentane	2.63	49.2
C-6/C-7	Benzene	5.70	80.1
C-7/C-8	2,2,4-Trimethyl-2-pentene	9.50	104.9
C-8/C-9	2,3,5-Trimethylhexane	14.83	131.3
C-9/C-10	3,3,5-Trimethylheptane	20.95	155.7

[1] Number of carbon atoms per molecule.

[2] Number of gasoline-range hydrocarbons evaluated.

[3] Retention times forming boundaries between carbon-number-sets on FID chromatograms.

[4] Boiling-points corresponding to retention-time limits.

[5] Percentage of hydrocarbon compounds expected to fall below the correct carbon-number set.

[6] Hydrocarbon compounds having retention-times and boiling-points near carbon-number-set boundaries which can be used as standards to divide chromatograms by carbon-number-increments.

Table 4. *Example carbon-number-analysis: comparison of four chromatograms*

[µg/L, micrograms per liter; std, standard; conc., concentration; ≤, less than or equal to; ≥, greater than or equal to]

	15 µg/L std[1]	V0206[2]	V0306[3]	V0506[4]
Number of peaks				
≤C5	3	1	1	1
C-6	3	4	5	0
C-7	3	6	8	3
C-8	2	12	14	3
C-9	4	10	15	5
≥C10	3	12	17	5
Conc. (µg/L)[1]				
≤C-5	28	347,546[5]	95,249[5]	8
C-6	28	293	223	0
C-7	50	1,153	1,986	14
C-8	31	1,756	4,316	15
C-9	47	893	1,692	21
≥C-10	46	653	1,334	22
Percent conc.[2]				
≤C-5	12.36	98.65	90.89	10.08
C-6	12.03	.08	.21	.00
C-7	21.79	.33	1.89	17.66
C-8	13.36	.50	4.12	18.80
C-9	20.63	.25	1.61	26.43
≥C-10	19.84	.19	1.27	27.05

[1] Calibration standard, 15 µg/L each of 16 hydrocarbon compounds in helium.

[2] Vapor sample from Galloway site: vapor probe 2, 6 feet deep.

[3] Vapor sample from Galloway site: vapor probe 3, 6 feet deep.

[4] Vapor sample from Galloway site: vapor probe 5, 6 feet deep.

[5] Methane peaks, probably from biological activity.

of this carbon-number-determination method is sufficient for semiquantitative chromatogram comparison.

Table 4 presents the results of carbon-number analysis of the chromatogram in figure 3 and three additional chromatograms. The chromatograms can be compared in terms of peak distribution. For gasoline hydrocarbons, the relative amounts of low-carbon-number and high-carbon-number compounds indicate the degree of weathering of the gasoline. Comparison of chromatograms in terms of the mass of each carbon number can show contaminant-attenuation effects, which can be used to study underground contaminant movement and dilution or results of remediation efforts. Thus, samples from different locations, or from the same location at different times, can be compared semiquantitatively.

SUMMARY

The methodology described uses GC with flame-ionization and thermal-conductivity detectors for analysis of hydrocarbons and inorganic gases. The chromatograph was located at an underground gasoline spill site and was used to analyze samples of unsaturated-zone gases. Placement of the chromatograph onsite eliminates the need for lengthy sample storage and transport, which are detrimental to vapor-phase sample integrity. Flame-ionization and thermal-conductivity detectors were used to characterize the soil-gas samples with respect to hydrocarbons and inorganic gases, respectively. A PE-Nelson data system was used to acquire and process the chromatographic data. Chromatographic data were analyzed by using a combination of specific-compound identification and carbon-number analysis. The latter

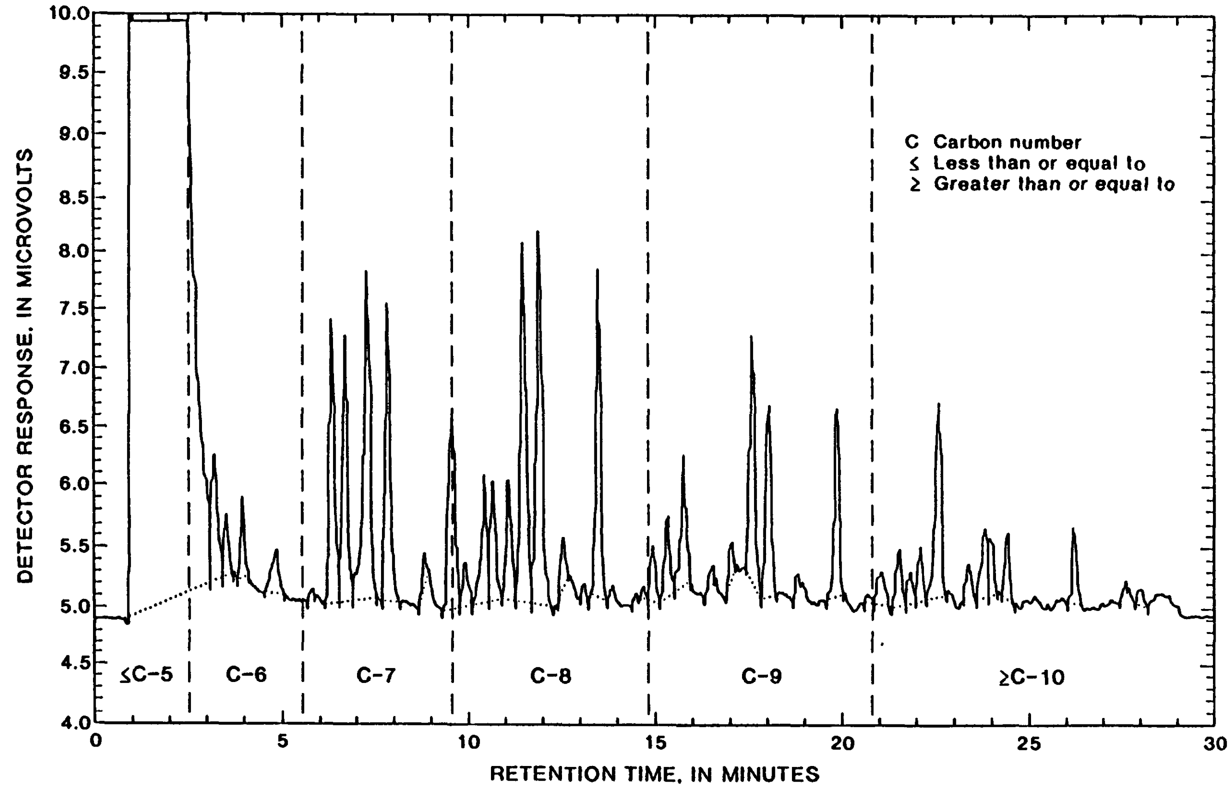

Figure 3. Flame ionization detector chromatogram of soil gas from Galloway Township vapor probe 2, 6 feet deep, partitioned by carbon number.

technique was developed to allow semiquantitative interpretation of complex FID chromatograms that contain numerous unidentified peaks.

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DISTRIBUTION OF ORGANIC AND INORGANIC CONSTITUENTS IN GROUND WATER AT GALLOWAY TOWNSHIP, NEW JERSEY

By Mary Jo Baedecker[1], Isabelle M. Cozzarelli[1], and Curtis S. Phinney[1]

ABSTRACT

Gasoline from a leaking storage tank on a farm in Galloway Township, New Jersey, resulted in the accumulation of free product in a shallow sand aquifer. Benzene, toluene, and the C_2-alkylbenzenes are the most soluble components of the gasoline and these compounds were found in a perched-water zone and in the water-table aquifer. Other components of the gasoline, the C_3- and C_4-alkylbenzenes and naphthalenes, were found in the water, and these compounds may remain longer in the aquifer than benzene, toluene, and the C_2-benzenes. The biodegradation of hydrocarbons by aerobic and anaerobic processes results in changes in the distributions of organic compounds and inorganic aqueous species in the perched-water zone and water-table aquifer. Differences in the geochemistry of water from these two water bodies are the result of movement of water and biogeochemical processes.

INTRODUCTION

Gasoline in ground water is one of the most widespread problems in subsurface contamination. The organic compounds from gasoline that are most commonly monitored in ground water are the aromatic hydrocarbons: benzene, toluene, and the C_2-alkylbenzenes (ethylbenzene and *o*-, *m*-, and *p*-xylene). The C_3- and C_4-alkylbenzenes (C_3 and C_4 refers to the number of carbon atoms attached to benzene) are less soluble in water but these compounds may be resistant to biodegradation and thus survive longer than other compounds in an aquifer (Eganhouse and others, 1987). Benzene and the alkylbenzenes are degraded in ground water by microbial activity under oxic and anoxic conditions (Barker and others, 1986; Cozzarelli and others, 1990).

Because some of the organic compounds in gasoline are soluble in water, a plume generally develops downgradient from the free product. The chemical composition of the plume is different from that of the native ground water. The concentrations of both organic and inorganic aqueous species change along a flow path in the plume. The processes that control the extent of contamination include the movement of ground water; dispersion, sorption, volatilization, and biodegradation of contaminants; and precipitation and dissolution of minerals. In shallow aquifers, microbial reactions are the most important processes in attenuating the concentrations of benzene and the alkylbenzenes (Barker and others, 1987). In field investigations in a shallow sand aquifer and laboratory experiments with the aquifer material, Barker and others (1987) found that hydrocarbons were biodegraded more slowly in anoxic environments than in oxic environments. Concentrations of most inorganic aqueous species increase above background levels in contaminant plumes. Exceptions are those chemical constituents that are reduced in oxidation-reduction reactions and, as a result, their concentrations decrease. This paper describes the processes that affect the distribution of organic compounds in a shallow aquifer and relates these processes to changes in the water chemistry.

Site Description

The study site is on a farm in Galloway, Township, N.J., about 10 miles west of Atlantic City. Gasoline leaked from a small underground storage tank, 2 to 6 ft (feet) below land surface, resulting in the accumulation of a nonaqueous phase product in a shallow aquifer. The tank was buried in the 1940's or 1950's and may have leaked for a long time. The sediment is mostly fine- to coarse-grained sand. Discontinuous clay lenses and iron oxide coatings are present in the upper 15 ft of the sands. The water table aquifer is 14 to 17 ft below land surface and the general direction of flow is to the east. Above the aquifer is a perched-water zone beginning about 10 ft below land surface. At the bottom of the perched zone is a clayey sand layer that is about 2 ft thick and 11 to 15 ft below land surface (Fischer and others, 1991, this Proceedings). Some dense clays as thick as a few inches were found near the bottom of the clayey sand. During part of this investigation, the area between the perched-water zone and the water-table aquifer was saturated because of high rainfall.

METHODS

Sampling Procedures

Water was collected from wells and probes from June 1989 to December 1990. The wells, 2 in. (inches) in diameter, were constructed of polyvinylchloride casings above the water table, stainless steel casings below the water table, and stainless-steel well screens with a 2-ft-long screened interval (fig. 1; U.S. Geological Survey wells). Some wells installed earlier were screened over a 15 ft interval (fig. 1; New Jersey Department of Environmental Protection wells). Water samples were collected with a peristaltic pump after evacuating the casing with three well-casing volumes. Teflon[2] tubing was used in the wells for sampling, and a short piece of silicone tubing (2 ft) was used through the pump head. Teflon tubing was dedicated to individual wells and silicone tubing was regularly changed to prevent cross contamination of water samples.

Water samples from more closely spaced intervals were collected from sampling probes of 1/4-in. stainless

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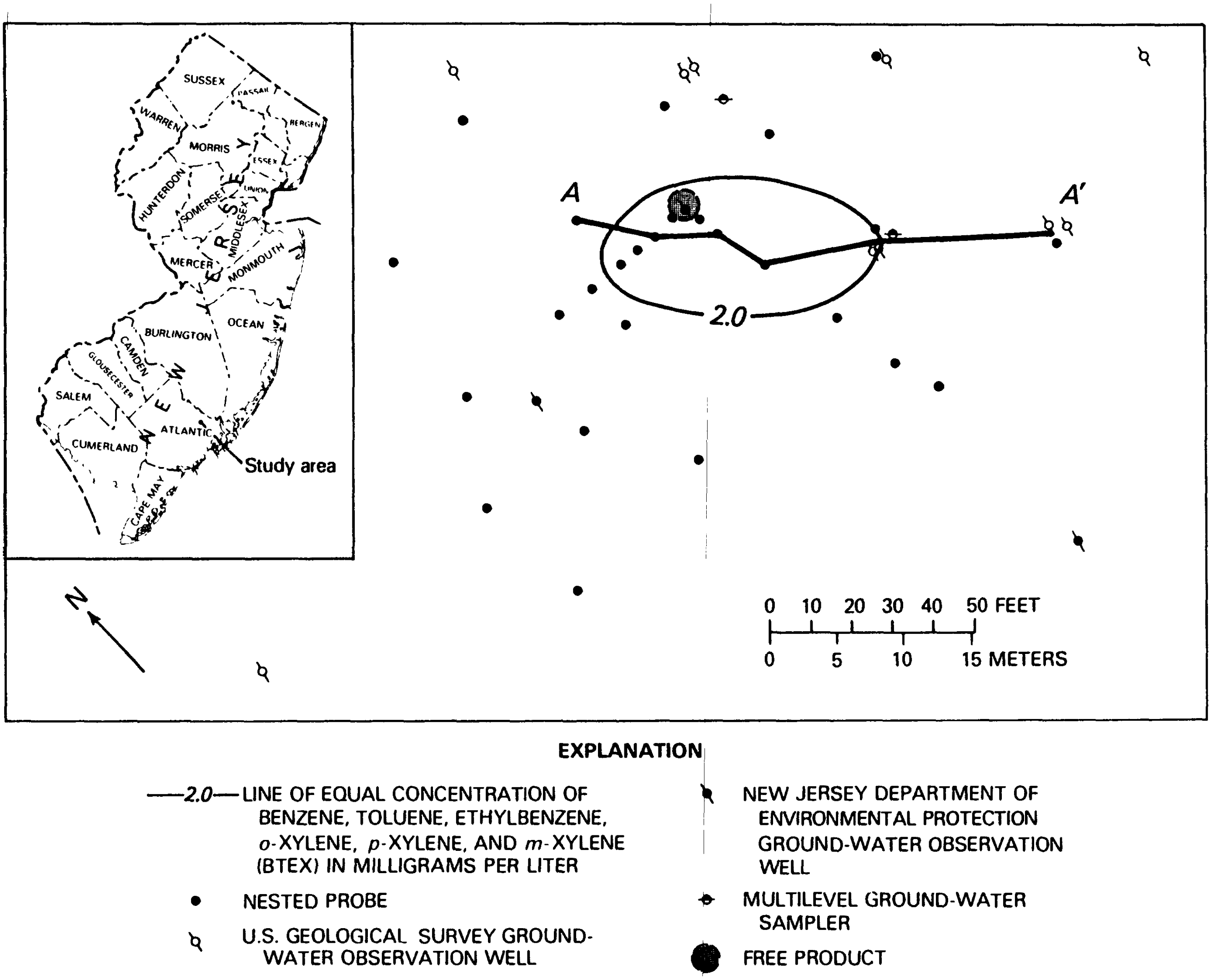
[1] U.S. Geological Survey, Reston, Va.

[2] Use of brand, firm or trade names in this paper is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.


SUSSEX
PASSAIC
WARREN
BERGEN
MORRIS
ESSEX
UNION
HUNTERDON
SOMERSET
MIDDLESEX
MERCER
MONMOUTH
OCEAN
BURLINGTON
CAMDEN
GLOUCESTER
SALEM
ATLANTIC
CUMBERLAND
CAPE MAY
Study area
N
A
A'
2.0
0 10 20 30 40 50 FEET
0 5 10 15 METERS
EXPLANATION
2.0 LINE OF EQUAL CONCENTRATION OF BENZENE, TOLUENE, ETHYLBENZENE, o-XYLENE, p-XYLENE, AND m-XYLENE (BTEX) IN MILLIGRAMS PER LITER
NESTED PROBE
U.S. GEOLOGICAL SURVEY GROUND-WATER OBSERVATION WELL
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MULTILEVEL GROUND-WATER SAMPLER
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Figure 1. Map of gasoline contaminated site in Galloway Township, New Jersey. Data (in milligrams per liter) are for benzene, toluene, ethylbenzene, and xylenes (BTEX), in water from the midsection of the perched-water zone, 11 to 14.5 feet below land surface, collected July 1990. Mean values are shown where more than one depth at a site was sampled. Transect A-A' is through the contaminated water.

steel that were screened over a 6-in interval (fig. 1; nested probes). Installation and construction of these probes is discussed in Fischer and others (1991, this Proceedings). The nested probes were sampled with a peristaltic pump attached directly to the stainless-steel tube with silicone tubing. Water was also sampled in July 1990 from an *in-situ* multiport sampler (fig. 1; multilevel sampler) described in Gibs and others (1991, this Proceedings).

Ground water was collected with a peristaltic pump and a Fultz submersible pump at one sampling location to determine the effect of using a peristaltic pump rather than a submersible pump to sample ground water. Two water samples were collected with each pump and then analyzed for aromatic hydrocarbons, including benzene, toluene, 16 alkylbenzenes, naphthalene and methyl naphthalenes. The results show that in water pumped with the peristaltic pump, the concentrations of benzene and toluene were higher by 21 and 3 percent, respectively, than in water pumped with the submersible pump. The concentrations of all other alkylbenzenes were lower by an average of 8.4 percent in water pumped with the peristaltic pump. Although these differences are significant, no advantage was found for using one pump or the other, and water samples were collected by a peristaltic pump. The nested probe samplers made of stainless-steel tubing could only be sampled with a peristaltic pump.

Analytical Procedures

Water samples were collected for organic and inorganic analyses. Measurements were made in the field for pH, temperature, dissolved oxygen (DO), and alkalinity (reported as bicarbonate). Analyses for those constituents that are sensitive to changes in redox were made using methods described in Baedecker and Cozzarelli (1991).

Major cations were determined by direct current plasma emission spectrometry on an ARL SpectraSpan V.

Samples were collected for the determination of aromatic hydrocarbons in 250 mL (milliliter) glass bottles and mercuric chloride was added as a preservative. The samples were spiked in the field with deuterated (d_{10}) orthoxylene, which was used as an internal standard. Recovery of this compound in laboratory experiments was 95.3 percent. In the laboratory, the samples were extracted with 2 mL pentane by shaking for 1.5 hours. The pentane extract was analyzed by gas chromatography with cryogenic focusing on a 30-meter long, 0.32 millimeter outside-diameter column, with a DB-Wax stationary phase with a film thickness of 0.25 micrometer (J and W Scientific). The column was installed in a Hewlett Packard Model 5890 II gas chromatograph equipped with a flame-ionization detector and a Dynamic Solutions Baseline data system. Quantitative data were obtained from the response factors of an external standard (containing 29 compounds) that was normalized to the internal standard (d_{10}-orthoxylene). Separate samples were analyzed on a Varian 3400 gas chromatograph interfaced to a Finnigan MAT Model 800 ion trap detector to verify identifications of compounds.

RESULTS AND DISCUSSION

The distributions of benzene, toluene, ethylbenzene, and *o*-, *m*-, and *p*-xylene (BTEX) were significantly different in the perched-water zone and water-table aquifer. In the midsection of the perched-water zone (11-14.5 ft below land surface) the concentrations of BTEX were greater than 2.0 mg/L (milligram per liter) in a small zone south of the source (fig. 1). The concentrations of BTEX decreased in all directions from this contaminated zone. From January to July 1990, the concentrations of BTEX in the perched- water zone were stable. The largest change in concentration was from 1.5 mg/L to 3.8 mg/L in water at the eastern edge of the contaminated zone.

In this same time period, the distributions of BTEX in the water table aquifer (20-26 ft below land surface) changed dramatically (fig. 2). The zone of highest concentrations (greater than 10 mg/L) shifted from the northern edge of the site in January 1990 to the south in July 1990. The concentrations of BTEX were as high as 29.2 mg/L in the most contaminated water. The hydraulic gradient is low in this part of the aquifer, about 0.004 to the east and, therefore, the movement of water is greatly affected by pumping of wells for farm use (Fischer and others, 1991, this Proceedings). This shift of contaminants may be caused by pumping of irrigation wells east of the site during the summer months.

Organic compounds other than BTEX are soluble components of the gasoline. The C_3- and C_4-alkylbenzenes were identified in all samples that contained BTEX. Fifteen of these compounds were identified and others are present that were only tentatively identified. Work is underway to separate and identify these compounds. In some parts of the aquifer, the C_3- and C_4- benzenes are more abundant than the BTEX assemblage. In the perched-water zone near the free product, the identified C_3- and C_4-benzenes were 82 percent of the total benzene and alkylbenzenes compared to 15 percent at a site in the water-table aquifer.

On a section (A-A' in fig. 1) northwest to southeast through the contaminated zone, the positions of the bottom of the perched-water zone and water table (fig. 3a) illustrate that these water bodies were continuous in July 1990, except on the northwestern side of the section where an intervening dry zone was encountered. Although the water was continuous between the perched-water zone and the aquifer, the clayey-sand zone is a semiconfining layer that hinders vertical mixing. The steep gradients in the concentrations of BTEX in ground water (fig. 3b) indicate that vertical mixing is hindered between the two water units. Areas of high concentrations of BTEX (greater than 5.0 mg/L) were found in both the perched-water zone and water-table aquifer.

The concentrations of DO show an area of anoxic ground water (fig. 4a) that is mostly in the perched-water zone. The pH measurements plot in a similar pattern to the DO concentrations (fig. 4b). The pH of uncontaminated water is acidic, 4.5 to 4.8, whereas the pH of contaminated water is generally higher (up to 6.11). The increase in pH in contaminated water may result from microbial degradation reactions that generate bicarbonate, which reacts with hydrogen ion to establish a bicarbonate-carbonic acid buffering system.

Data for pH, inorganic aqueous species, and some organic compounds indicate that several processes are affecting the water chemistry in the contaminated ground water as compared to uncontaminated ground water (table 1). In the contaminated water (perched-water zone and water-table aquifer), concentrations of DO, nitrate

Table 1. *Chemical constituents at three locations in a sand aquifer, Galloway Township, New Jersey*

[Values are in milligrams per liter, except for pH; <, less than; --, no data; BDL, below detection limit]

	Uncontaminated perched water	Contaminated perched water	Contaminated ground water
pH	4.73	5.99	5.15
DO	6.09	0	.37
NH_4^+	BDL	1.98	.25
Fe^{2+}	BDL	37.0	1.17
Mn^{2+}	.062	.333	.022
Ca^{2+}	13.2	18.6	8.85
Mg^{2+}	3.6	4.5	1.97
Na^+	7.9	7.4	2.82
K^+	3.5	5.5	4.86
Sr^{2+}	.048	.049	.035
Si	2.4	1.15	1.39
Al^{3+}	.26	.023	.125
HCO_3^-	2.44	174	17.1
NO_3^-	39.7	BDL	BDL
SO_4^{2-}	23.7	2.91	24.4
Cl-	8.9	6.88	.443
H_2S	BDL	1.10	BDL
CH_4	BDL	.0066	--
Benzene	BDL	.22	8.04
Toluene	BDL	2.87	9.55
Ethylbenzene	BDL	1.22	1.31
o-xylene	BDL	2.43	2.93
m-xylene	BDL	4.88	5.27
p-xylene	BDL	2.09	2.11
TAH[1]	<.002	20.3	34.2

[1] Total aromatic hydrocarbons (TAH) includes benzene, toluene, C2-benzenes, 15 C3-and C4-benzenes, napthalene, and methyl naphthalenes.

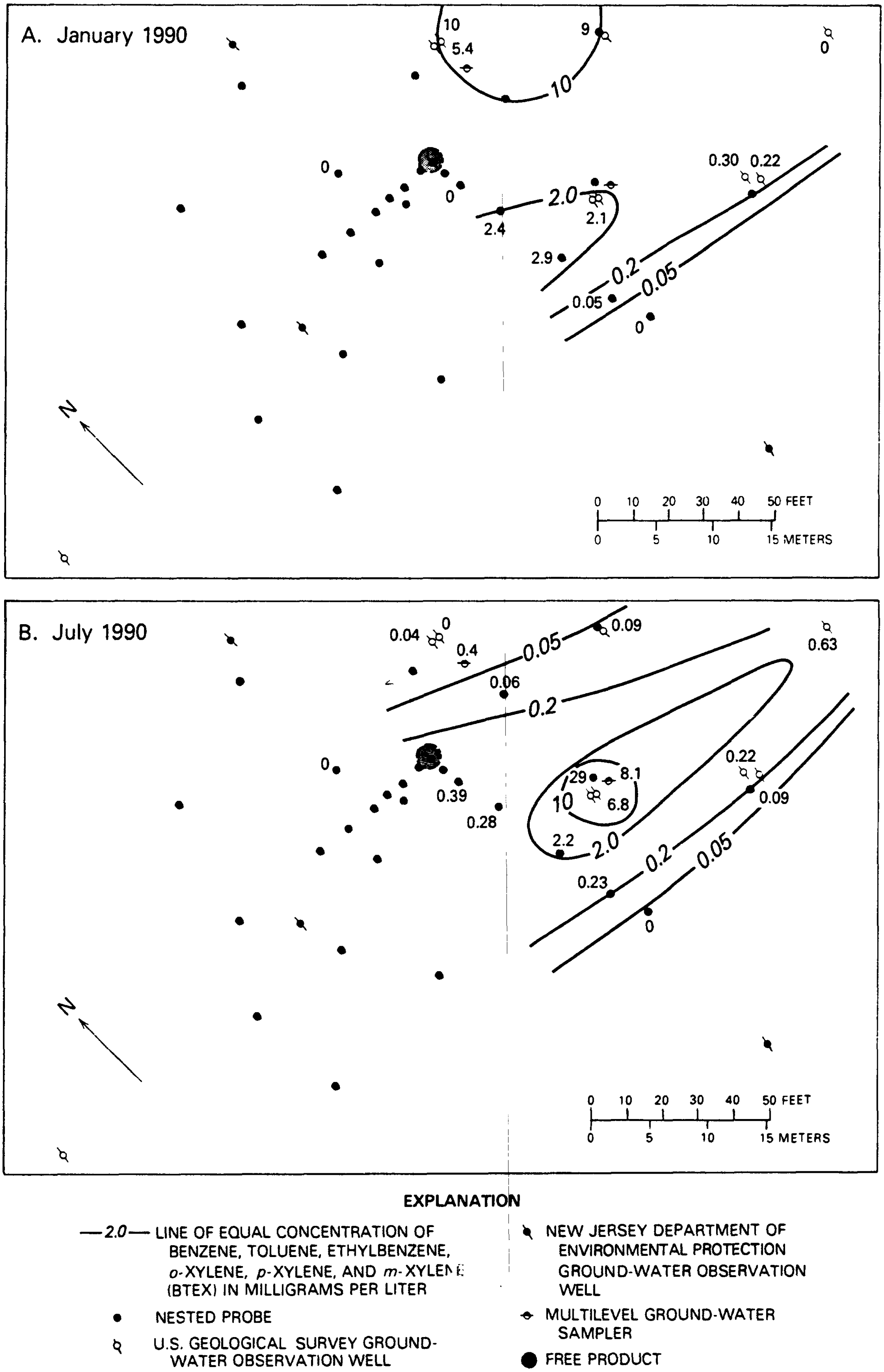
A. January 1990
10
5.4
9
0
10
0
0
2.0
2.1
2.4
2.9
0.30
0.22
0.2
0.05
0.05
0
N
0 10 20 30 40 50 FEET
0 5 10 15 METERS
B. July 1990
0.04
0
0.4
0.05
0.09
0.63
0.06
0.2
0
0.39
0.28
29
8.1
10
6.8
2.2
2.0
0.22
0.09
0.23
0.2
0.05
0
N
0 10 20 30 40 50 FEET
0 5 10 15 METERS
EXPLANATION
—2.0— LINE OF EQUAL CONCENTRATION OF BENZENE, TOLUENE, ETHYLBENZENE, o-XYLENE, p-XYLENE, AND m-XYLENE (BTEX) IN MILLIGRAMS PER LITER
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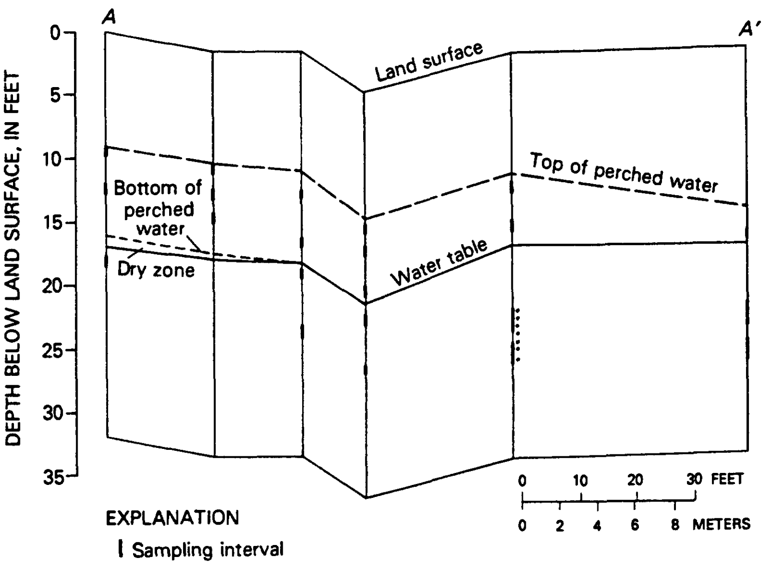
Figure 2. Maps showing data (in milligrams per liter) for benzene, toluene, ethylbenzene, and the xylenes (BTEX), in water from the water-table aquifer, at depth of 20 to 26 feet below land surface, collected (a) January 1990 and (b) July 1990. Mean values are shown where more than one depth at a site was sampled.

A. Fence diagram


DEPTH BELOW LAND SURFACE, IN FEET
0
5
10
15
20
25
30
35
A
A′
Land surface
Top of perched water
Bottom of perched water
Dry zone
Water table
0 10 20 30 FEET
0 2 4 6 8 METERS
EXPLANATION
Sampling interval

B. BTEX, July 1990

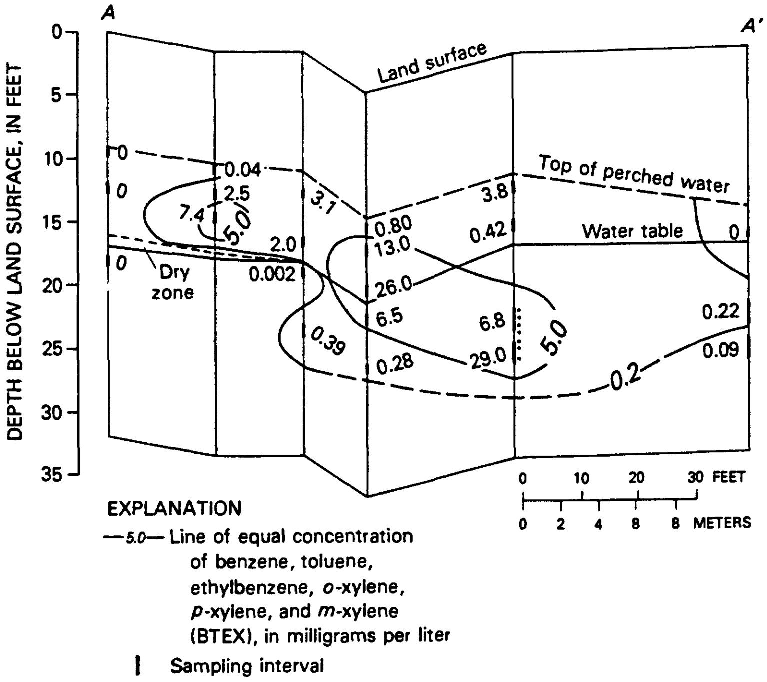
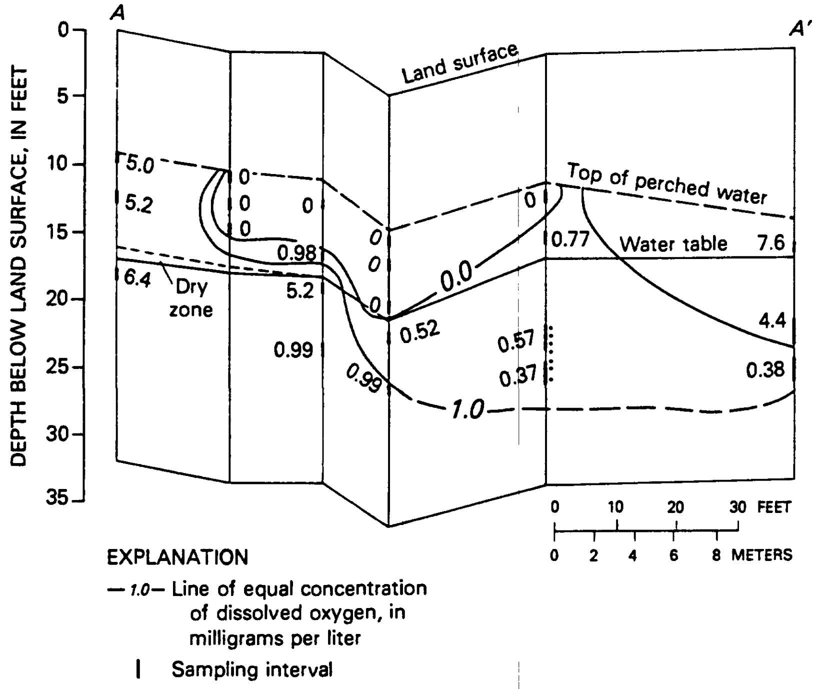


Figure 3. Section along transect A-A′ (fig.1) showing for July 1990 (a) the location of the perched-water zone surface, the base of the perched unit, the water table, and the location and length of screened interval for sampling points; (b) the distribution of benzene, toluene, ethylbenzene, and the xylenes (BTEX) (in milligrams per liter) in ground water.

A. Dissolved oxygen, July 1990


A
A'
DEPTH BELOW LAND SURFACE, IN FEET
0
5
10
15
20
25
30
35
Land surface
Top of perched water
Water table
5.0
5.2
6.4
Dry zone
0
0
0
0
0.98
5.2
0.99
0
0
0
0.99
0.0
0.52
0.57
0.37
1.0
0
0.77
7.6
4.4
0.38
0 10 20 30 FEET
0 2 4 6 8 METERS
EXPLANATION
—1.0— Line of equal concentration of dissolved oxygen, in milligrams per liter
Sampling interval

B. pH, July 1990

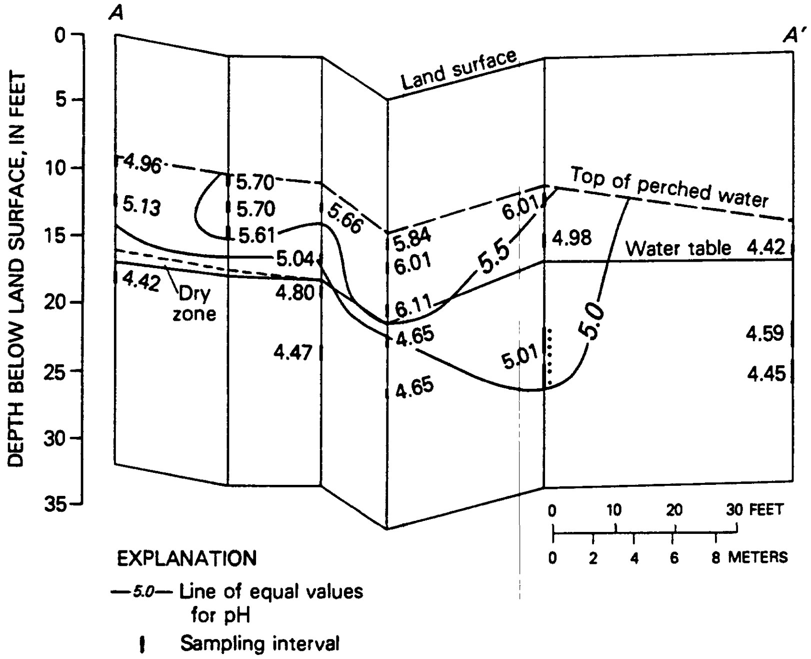

A
A'
DEPTH BELOW LAND SURFACE, IN FEET
0
5
10
15
20
25
30
35
Land surface
Top of perched water
Water table
4.96
5.13
4.42
Dry zone
5.70
5.70
5.61
5.04
4.80
4.47
5.66
5.84
6.01
6.11
4.65
4.65
5.5
6.01
5.01
5.0
4.98
4.42
4.59
4.45
0 10 20 30 FEET
0 2 4 6 8 METERS
EXPLANATION
—5.0— Line of equal values for pH
Sampling interval

Figure 4. Section along transect A-A' (fig. 1) showing the distributions of (a) dissolved oxygen (in milligrams per liter) and (b) pH in ground water.

(NO_3^-), and sulfate (SO_4^{2-}) are lower, and concentrations of bicarbonate (HCO_3^-), ammonia (NH_4^+), and ferrous iron (Fe^{2+}) are higher than in the uncontaminated water. Hydrogen sulfide (H_2S) was found in the perched-water zone and was below detection limit or in trace amounts in the water-table aquifer. Concentrations of methane (CH_4) were above detection limit, but the values were low (less than 0.01 mg/L) suggesting that methanogenesis is not an important process at this site. Concentrations of the major cations other than Fe^{2+} were about the same in the contaminated and uncontaminated water. This indicates that ion exchange reactions are of minor importance. Aerobic respiration and microbially mediated reduction of NO_3^-, SO_4^{2-}, and iron oxides are the major processes that affect the water chemistry. These reactions have occurred to a greater extent in the perched-water zone than in the water-table aquifer. In the water-table aquifer the concentrations of DO and SO_4^{2-} are less depleted than in the perched-water zone and the concentrations of the products of organic degradation reactions (HCO_3^-, NH_4^+, Fe^{2+}, and H_2S) are lower. Also, the water is farther from equilibrium in the water-table aquifer than in the perched-water zone. This is supported by the simultaneous presence of Fe^{2+}, DO, and, in some locations, H_2S, in the water-table aquifer. Detailed geochemical processes that occur in a vertical profile are described by Cozzarelli and others (1991, this Proceedings).

The organic compounds, benzene and toluene, are more easily biodegraded than the C_2-, C_3- and C_4-benzenes. Benzene and toluene comprise 15.2 percent of the total aromatic hydrocarbons in the perched-water zone and 51.4 percent in the water-table aquifer (table 1). This indicates a loss of benzene and toluene and preferential accumulation of the C_2-, C_3- and C_4-benzenes in the perched-water zone. This loss is a result of biodegradation, and possibly, of volatilization of benzene and toluene.

SUMMARY

Aromatic hydrocarbons are the major organic compounds found in ground water at a site contaminated with free product from a leaking storage tank. The compounds BTEX are the most soluble components of the gasoline. These compounds are biodegraded by aerobic and anaerobic processes that change the water chemistry. Other compounds that include the C_3- and C_4-alkylbenzenes and naphthalenes are present in the water and these compounds may remain longer in the water-table aquifer than the compounds BTEX. In the contaminated water, the pH and concentrations of HCO_3^-, NH_4^+, Fe^{2+}, and H_2S increased and concentrations of DO, NO_3^-, and SO_4^{2-} decreased. The differences in water chemistry of the perched-water zone and the water-table aquifer may result from the amount of microbial activity and volatilization that has occurred.

The free product originally accumulated in the perched zone from the leaking storage tank that was about 2 to 6 ft below land surface. The tank was buried in the 1940's or 1950's and may have leaked for a long time. Therefore, the microbiological community and geochemical reactions in the perched-water zone may have evolved to a relatively stable environment that is affected by rainfall and temperature. It is possible that free product came in contact with the water table at a later time and that a stable environment in the water-table aquifer is yet to be established. Geochemical data presented here indicate that the water is out of equilibrium. Also, the low ground-water hydraulic gradient in the local area hinders the development of a plume. The direction of movement of contaminated ground water is generally east but is affected by the pumping of wells locally. The north- south movement of the contaminated water may have prevented establishment of a stable biogeochemical environment in the water-table aquifer.

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NON-FICKIAN VAPOR TRANSPORT IN SAND COLUMNS CONTAMINATED WITH VOLATILE ORGANIC COMPOUNDS

By Clifford J. Bruell[1], Craig D. Gilbert[1], and Arthur L. Baehr[2]

ABSTRACT

The vapor-phase component of a highly volatile organic compound in a porous medium may exceed the constraint of a dilute species diffusing in a bulk phase assumed by Fick's Law. The Stefan- Maxwell equations provide a more general model for quantifying steady-state vapor diffusion of volatile organic substances. Experimental soil-column diffusion data show that a Fickian-based model overestimated soil tortuosity by 35 percent and failed to account for the displacement of atmospheric gases (for example, oxygen) by the diffusing volatile organic compound. Therefore, use of the Fickian-based model can lead to an erroneous interpretation of soil-gas data if depleted oxygen levels are attributed to microbial degradation.

This document describes a part of the work accomplished under U.S. Geological Survey Cooperative Agreement Number 14-08-0001-A0688; and University of Lowell Research Foundation Project Number 05 5315.

November 30, 1990

INTRODUCTION

Analyzing the transport of volatile organic compounds in the unsaturated zone is difficult because of the complexities inherent in considering the gas phase. Traditionally, the simulation of vapor-phase diffusion in porous media has been accomplished by using Fick's Law (Weeks and others, 1982; Baehr, 1987). Fick's Law is valid for the diffusion of a dilute species into a bulk phase. When a volatile organic liquid is present in a porous medium, however, the concentration of the organic component in the associated vapor phase can violate the dilute-species constraint of Fick's Law. As an alternative to using Fick's Law, the Stefan-Maxwell equations provide a more comprehensive model for quantifying steady-state transport for a vapor phase composed of any parts of its constituents (Baehr and Bruell, 1990).

Laboratory-scale unsaturated-soil-column experiments were conducted to investigate diffusive vapor transport of volatile organic compounds in porous media. The results of this research will be used to develop and calibrate a modular, multiphase, and compositional mathematical model of volatile-organic-contaminant transport and biodegradation. This paper presents part of that research, focusing on (1) the design of an experimental soil-column apparatus and development of analytical techniques, and (2) a selected experiment that demonstrates the use of these methods and materials to examine non-Fickian steady-state vapor-phase diffusion.

BACKGROUND AND THEORY

The Stefan-Maxwell equations have been used by chemical engineers to describe concentration-dependent vapor diffusion (Bird and others, 1960). The background material presented here, which describes the application of the Stefan-Maxwell equations for the analysis of vapor-phase diffusion in porous media, is based on a publication by Baehr and Bruell (1990).

The Stefan-Maxwell equation describing diffusion of a multicomponent gas phase is as follows:

$$\nabla \chi_k = \sum_{\substack{i=1 \\ i \neq k}}^{M} \frac{1}{cD_{ki}} \left(\chi_k \frac{J_i}{\omega_i} - \chi_i \frac{J_k}{\omega_k} \right) \qquad (1)$$

$$k = 1, 2, ..., M$$

where

χ_k is the mole fraction of the k^{th} constituent,

c is the vapor-phase molar density ($c = 4.46 \times 10^{-5}$ moles per cubic centimeter for an ideal gas at standard temperature and pressure),

D_{ki} is the diffusion coefficient (square centimeters per second) in the porous medium for a binarly vapor phase consisting of constituents k and i,

J_i is the total mass flux of the i^{th} constituent (grams per square centimeter-second) and

ω_i is the molecular weight of the i^{th} constituent (grams per mole).

Diffusion coefficients in the porous medium are related to bulk-phase diffusion coefficients as follows:

$$D_{ki} = D_{ki}^{b} \ \theta_a \tau \qquad (2)$$

where

D_{ki}^{b} is the binary diffusion constant (without porous media) composed of constituents k and i,

θ_a is air-filled porosity, and

τ is the tortuosity of the vapor-filled pores. The method of Fuller and others (1966) was used to calculate the binary diffusion constant, D_{ki}^{b}.

Diffusion experiments were conducted in a vertical soil column oriented above a liquid-phase hydrocarbon reservoir (fig. 1), where distance from the reservoir is represented by z (centimeters). The analysis of this system is based on a three-constituent version of equation 1. Only the organic constituent evaporating from the liquid reservoir (k=1) has a significant flux, as the major constituents of air, O_2 and N_2 (k=2, 3, respectively), have insignificant solubility in the liquid organic material contained within the reservoir.

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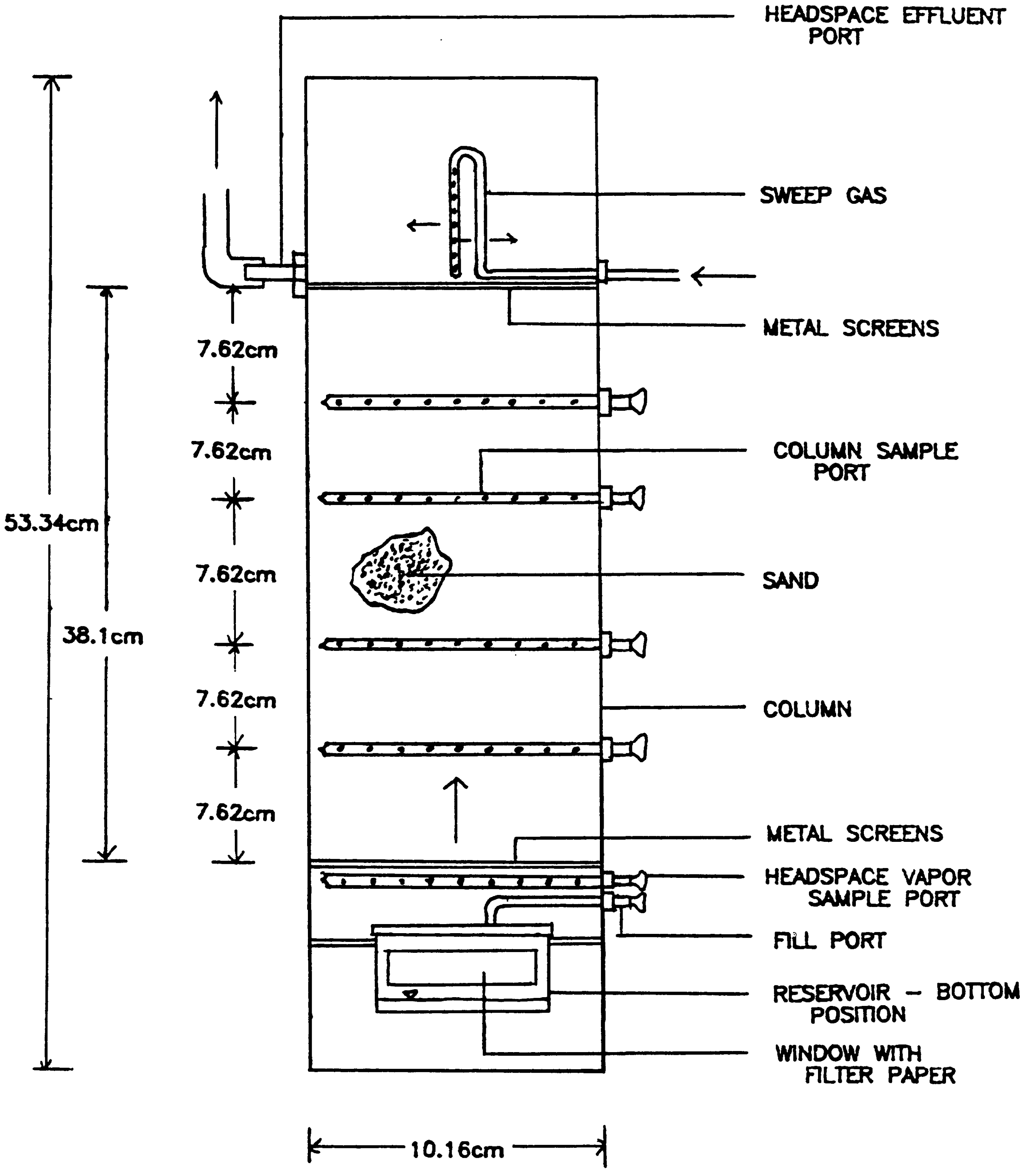
HEADSPACE EFFLUENT PORT
SWEEP GAS
METAL SCREENS
COLUMN SAMPLE PORT
SAND
COLUMN
METAL SCREENS
HEADSPACE VAPOR SAMPLE PORT
FILL PORT
RESERVOIR - BOTTOM POSITION
WINDOW WITH FILTER PAPER
53.34cm
38.1cm
7.62cm
7.62cm
7.62cm
7.62cm
7.62cm
10.16cm

Figure 1. Experimental soil diffusion column.

Therefore, $J_k = 0$ for $k = 2, 3$ and equation 1 reduce to the following system of ordinary differential equations defining the mole fractions χ_k as a function of column distance (depth) z:

$$\frac{d\chi_1}{dz} = -a\left(\frac{\chi_2}{D_{12}{}^b} + \frac{\chi_3}{D_{13}{}^b}\right) \tag{3a}$$

$$\frac{d\chi_2}{dz} = \frac{a}{D_{12}{}^b}\chi_2 \tag{3b}$$

$$\frac{d\chi_3}{dz} = \frac{a}{D_{13}{}^b}\chi_3 \tag{3c}$$

subject to the following boundary conditions:

$$\begin{aligned}\chi_1(z=0) &= \chi_1^0 = 1 - \chi_2^0 - \chi_3^0\\ \chi_2(z=0) &= \chi_2^0\\ \chi_3(z=0) &= \chi_3^0\end{aligned}$$

where $a = \frac{1}{c\theta_a\tau}\frac{J_1}{\omega_1}$.

The solution to system (3a) - (3c) is

$$\chi_1 = 1 - \chi_2 - \chi_3 \tag{4a}$$

$$\chi_2 = \chi_2^0\exp\left(\frac{az}{D_{12}{}^b}\right) \tag{4b}$$

$$\chi_3 = \chi_3^0\exp\left(\frac{az}{D_{13}{}^b}\right). \tag{4c}$$

Fick's Law is defined as follows:

$$J_1 = -c\omega_1 D_1^b\,\theta_a\tau_F\frac{d\chi_1}{dz} \tag{5}$$

where

D_1^b is the diffusion coefficient of the organic constituent in air and

τ_F is the estimate of tortuosity in a Fickian analysis.

METHODS AND MATERIALS

The column was designed to minimize leakage, and materials of construction were selected to minimize hydrocarbon adsorption. The column was constructed from 10.16-cm (centimeter) inside-diameter (ID) schedule 40 aluminum pipe (6061-T6). A total of four vapor-sample ports are located in the soil at 7.62-cm intervals along the column axis and one is immediately adjacent to the screen in the reservoir headspace vapor (HSV) chamber. Headspace effluent (HSE) sweep-gas concentrations are measured at the HSE port. A liquid-sample reservoir made from an aluminum soil-sampling can is used to hold the organic liquid. The aluminum can is capped and filled through ⅛-in. (inch) metal tubing that enters the cup through a hole in the cap. A 1.5-cm window is cut around the circumference of the can to allow the organic vapors to escape. The interior of the can is lined with filter paper to aid in the evaporation of the liquid and to help prevent liquid from spilling out the side of the reservoir. A combination of insert rings, perforated metal soil-support screens, and a 200-mesh stainless-steel wire cloth were used at both ends of the column to support the soil within the column. The column and insert rings were machined to maintain a constant ID throughout the column.

Soil-gas samples were removed from vapor-sampling ports within the soil column. These ports are made from ⅛-in. aluminum tubing and the rest of the fittings are made of either brass or stainless steel. Glass end caps are held in place with Teflon[3]-gasketed clamps. In order to minimize the adsorption of hydrocarbons, these gaskets are covered with reagent grade, oil-free aluminum foil prior to assembly.

A coarse concrete-sand fraction from a Connecticut glacial alluvial deposit was used in this experiment. The sand was sieved, and the American Society for Testing Materials (ASTM) 16-30 mesh fraction was used. The columns, components, and sand were cleaned and heated to 105 °C (degrees Celsius) for a minimum of 12 hours prior to assembly to remove any hydrocarbon residue and to minimize biological growth.

Soil columns were filled with approximately 3,100 cm^3 (cubic centimeters) of dry sand. The remaining volumes above and below the soil column were each 760 cm^3. The sand was added in 700-cm^3 increments through a plastic tube. Uniform compaction was ensured by periodic column vibration on a vibration table.

Sweep gas consisting of air flow of 79.4 milliliters per minute was maintained at the end of the column opposite the liquid organic reservoir. Compressed air from a portable 1 horsepower oilless compressor was metered to the column through two in-line pressure regulators and a needle valve. Sweep gas was passed first through an indicating silica-gel dryer, then through an airstone immersed in 400 mL (milliliters) of deionized water in a 500-mL Erlenmeyer flask. To moisten the soil, water-saturated air was passed through the soil column for a minimum of 24 hours. During the experiments, the columns and sweep-gas flow-control apparatus were located in an environmental chamber maintained at 20 °C.

A gas chromatograph (GC) was used to quantify methylene chloride ($MeCl_2$), N_2, and O_2 in column soil-gas samples. The GC was equipped with a heated gas-sampling valve, a flame-ionization detector (FID), and a thermal-conductivity detector (TCD). The system was configured to allow the simultaneous analysis of all three species ($MeCl_2$, O_2, N_2) with one sample injection. One sample is loaded into two 0.1-cm^3 sample loops within the gas-sampling valve. Upon injection the contents of the loops are directed onto two separate analytical columns. A 10-ft(foot)-by-⅛ -in. stainless-steel column packed with AT-1200 and 1.75-percent Bentone 34, on Chrom-W-AW (100/120 mesh), with an N_2 carrier-gas flow rate of 24 cm^3/min (cubic centimeters per minute), was connected to the FID for the analysis of $MeCl_2$. An 8-ft-by-⅛ in. stainless-steel column packed with Carbosphere (80/100 mesh), with a helium carrier-gas flow rate of 40 cm^3/min, was connected to the TCD for the analysis of O_2 and N_2. System temperatures were maintained as follows: gas-sampling loop

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[3] The use of brand, firm, or trade names in this paper is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

100 °C, FID 180 °C, and TCD 300 °C. Oven temperature program was as follows: initial, 35 °C for 5 minutes; ramp, 35 °C per minute; and final, 70 °C for 8 minutes.

The syringes were purged with five volumes of ultra-pure carrier-grade (UPC) helium immediately prior to sample collection. The syringe dead volume was purged with 0.8 cm^3 of sample, and then a 2.6-cm^3 sample was collected. For the preparation of external standard curves, $MeCl_2$ vapor standards at concentrations less than saturation were prepared by adding weighed quantities of $MeCl_2$ to a 1-liter gas-sampling bulb filled with air. To prepare O_2 and N_2 standard curves, samples of dried air at atmospheric pressure and ambient temperature were diluted with varying volumes of UPC helium in a gas-sampling bulb. O_2 and N_2 concentrations in ambient air were determined by using the ideal-gas law and tabulated values of the mole percentages of normal atmospheric components.

NON-FICKIAN VAPOR TRANSPORT

Steady-state soil-column diffusion experiments were conducted for $MeCl_2$ with liquid organic reservoir located beneath the column. Experiments were run in duplicate and were highly reproducible. Results from only one column, with a total soil porosity of 40 percent, are presented here, however. Following the addition of the $MeCl_2$ to the reservoir, columns were allowed to achieve steady-state vapor concentrations with water-saturated sweep gas flowing across the soil surface prior to sampling. A constant diffusive flux experimentally measured at the soil surface served as the criterion for steady-state conditions. These conditions were achieved within 48 hours. Experimental measurements of $MeCl_2$, O_2, and N_2 concentrations were made at each sampling port within the soil column and are presented in figures 2, 3, and 4, respectively. At the soil surface a sweep-gas flow rate of 79.4 cm^3/min and a $MeCl_2$ flux of 1.772 x 10^{-8} moles per square centimeter per second were measured.

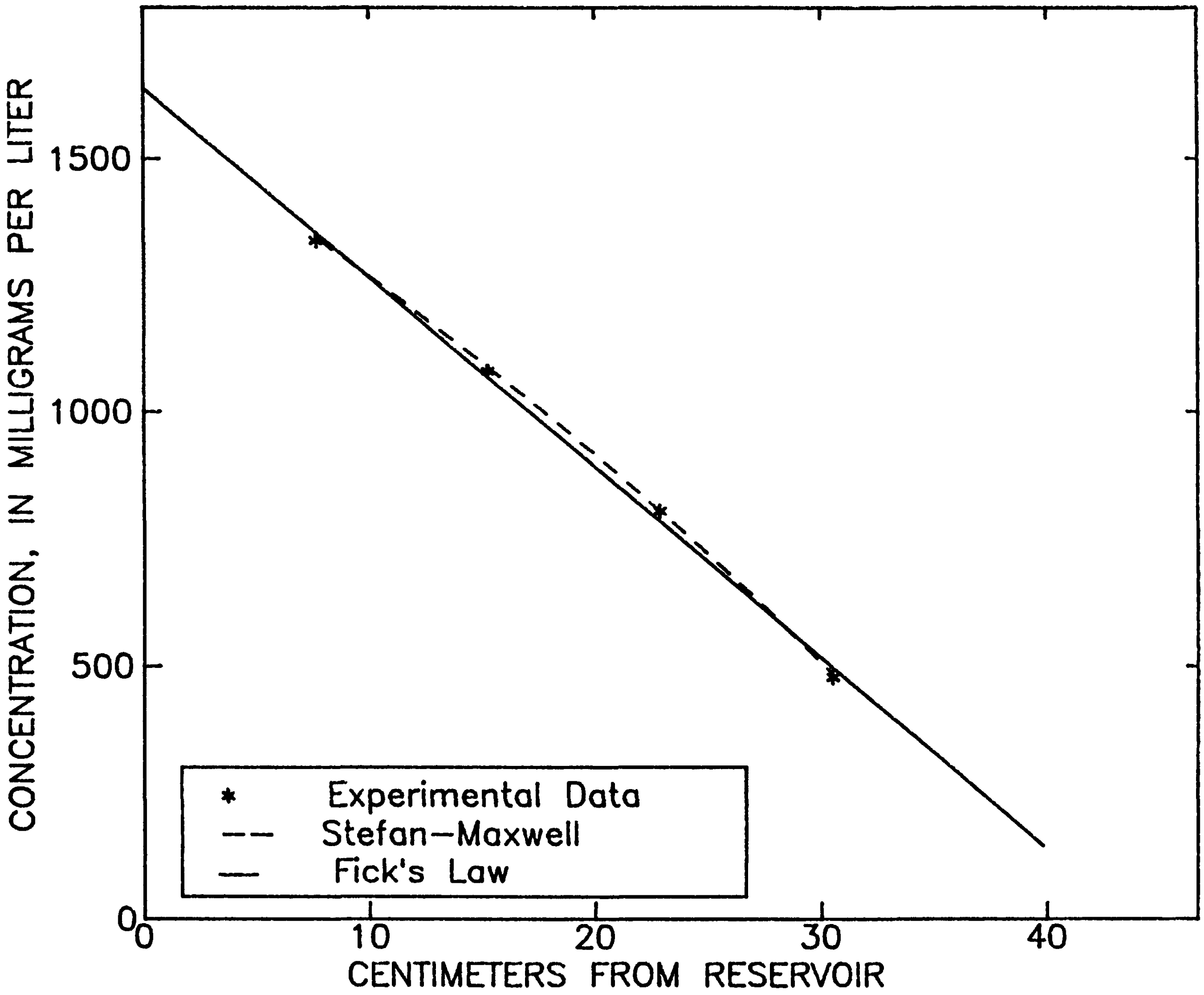

Figure 2. Methylene chloride concentration as a function of soil column depth, experimental data and as predicted by Fick's Law and Stefan-Maxwell model.

Theoretically predicted curves for $MeCl_2$, O_2, and N_2 were produced by using the Stefan-Maxwell equations and are presented in the corresponding figures. As predicted by the Stefan-Maxwell equations, experimental data show curvilinear concentration gradients for $MeCl_2$, O_2, and N_2. Experimental data show good agreement with the predicted Stefan-Maxwell curves; in no case is the difference greater than 1 percent.

Fick's Law theoretically predicts a linear concentration gradient for $MeCl_2$, as shown in figure 2. $MeCl_2$ experimental data depart form the linear prediction of Fick's Law. Fick's Law does not predict the distributions of O_2 or N_2 within the soil column.

Fick's Law steady-state solution to equation 5 is linear and the slope of the regression line was fitted to the experimental data to calculate $\tau_F = 0.985$. Calibration of the Stefan-Maxwell model prediction χ_1, defined by equations 4a to 4c by using a least-squares criterion, yielded the estimate of $\tau_{S\text{-}M} = 0.725$. Although Fick's Law provides a good fit to the data (linear correlation coefficient of 0.9984), the Fick's Law estimate of tortuosity is significantly higher than the Stefan-Maxwell estimate. The relative error, as defined by $(\tau_F - \tau_{S\text{-}M})/\tau_{S\text{-}M}$, is 35.8 percent. In this case, Fick's Law provides an appropriate empirical model for the transport of a single constituent at the experimental condition; however, it is not appropriate for estimating tortuosity.

The Stefan-Maxwell model predicts concentration gradients for O_2 and N_2 resulting from physical displacement by $MeCl_2$. Displacement of O_2 and N_2 is demonstrated in figures 3 and 4, respectively. A Fick's Law model does not incorporate this compositional coupling and predicts constant atmospheric concentration of O_2 and N_2 throughout the column because there is no flux of these gases. If Fick's Law is assumed to describe the flux of O_2, then an apparent sink (for example, the aerobic microbial degradation of $MeCl_2$) might be erroneously assumed to account for the observed decrease in the concentration of soil gaseous O_2 in the vicinity of a volatile-organic-compound source.

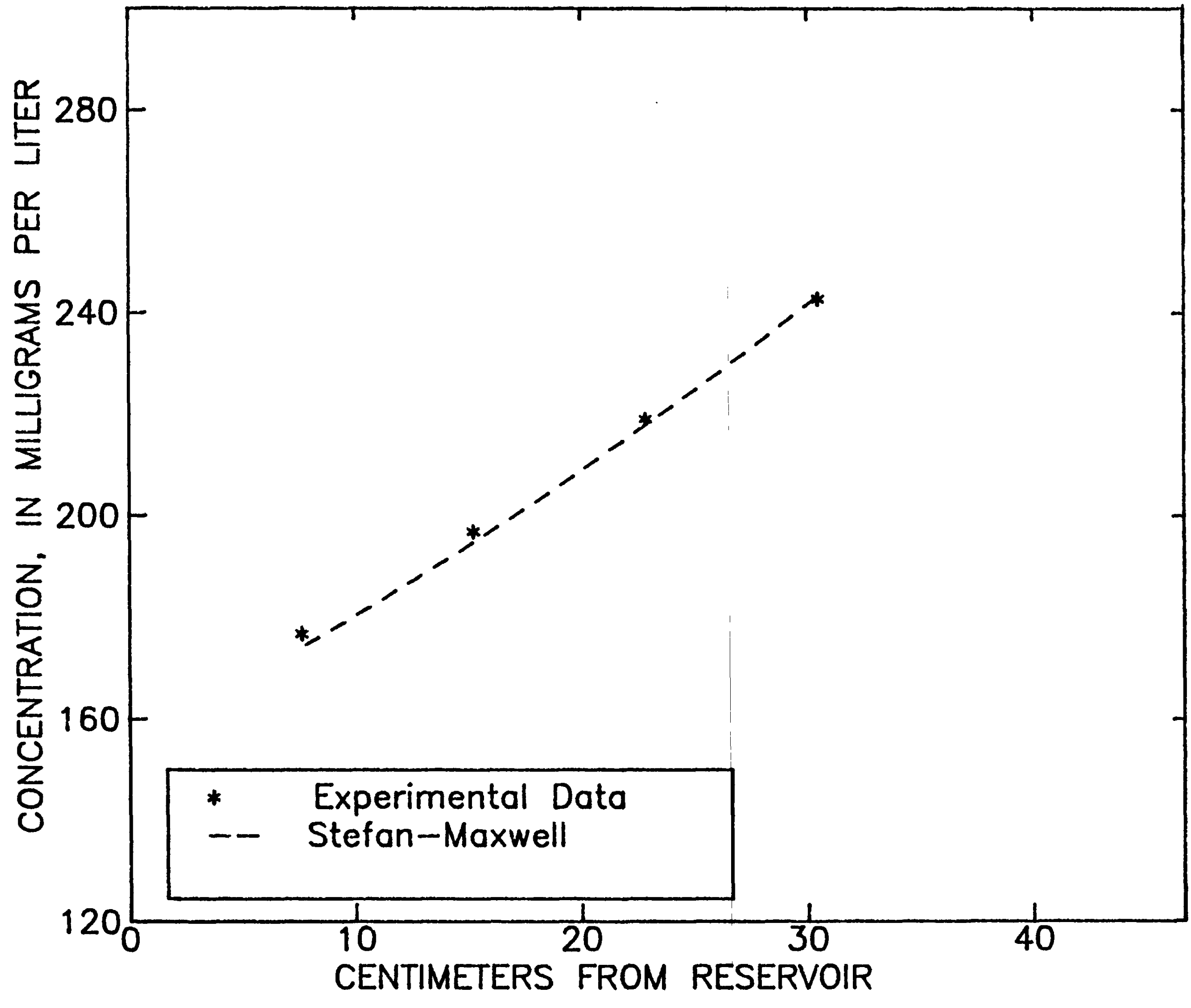

Figure 3. Oxygen concentration as a function of soil column depth.

Use of the Stefan-Maxwell equations should be incorporated in transport models for highly volatile organic materials. Furthermore, coupling of biodegradation models with these considerations will ensure that spatial changes in the concentrations of electron acceptors (for example, oxygen when considering the aerobic degradation of hydrocarbons) are not improperly attributed to biodegradation.

SUMMARY

An understanding of the diffusive behavior of vapor-phase volatile organic compounds is necessary for simulating their transport in soils. In this study, an examination of the soil-vapor diffusion of a highly volatile organic compound (methylene chloride) was conducted by using soil columns. The vertically oriented columns were constructed of 10.16-cm-ID aluminum pipe and contained a 38.1-cm soil column on a support screen located above a suspended reservoir filled with methylene chloride. Sampling ports were located below the support screen, along the length of the soil column, and in the headspace above the soil. The headspace was flushed continuously with a measured amount of sweep gas (that is, air) at a constant flow rate. The column design allowed for the measurement of hydrocarbon concentrations within the soil column and hydrocarbon flux at the soil surface.

A constant diffusive flux experimentally measured at the soil surface served as the criterion for steady-state conditions. These conditions were achieved within 48 hours following filling of the column reservoir with methylene chloride. Under steady-state conditions experimental measurements of $MeCl_2$, O_2, and N_2 vapor-phase concentrations were made throughout the soil column.

Vapor-phase composition was simulated by using Fick's Law, which assumes a dilute species and does not consider displacement of O_2 and N_2. Soil tortuosity was overestimated when Fickian diffusion was assumed. Fick's Law has limitations when used to simulate steady-state transport of highly volatile organic substances when contaminant constituents become dominant components of

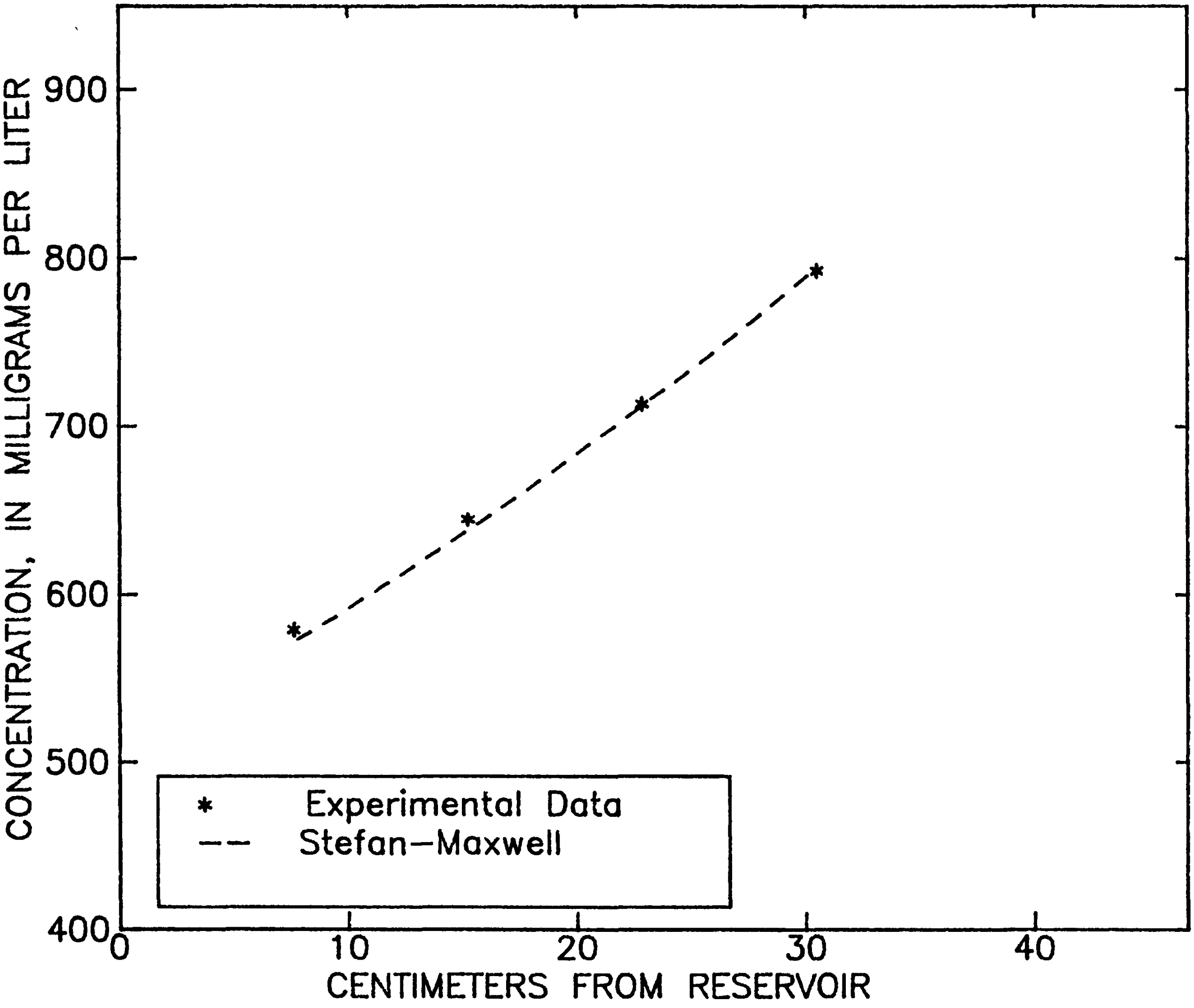

Figure 4. Nitrogen concentration as a function of soil column depth.

the vapor phase. A serious limitation of Fick's Law is its inability to simulate physical displacement of atmospheric gases (for example, O_2 and N_2) by the organic constituent. Use of a Fickian-based model could lead to misinterpretation of soil-gas data by the erroneous attribution of depleted O_2 levels to a sink term, such as aerobic microbial degradation.

The composition of the vapor phase was simulated accurately by using the Stefan-Maxwell equations, which do consider O_2 and N_2 displacement. The compositional model given by the Stefan-Maxwell equations is more useful than one based on Fick's Law for analyzing this problem.

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OVERVIEW OF NONPOINT-SOURCE CONTAMINATION OF THE HIGH PLAINS AQUIFER IN SOUTH-CENTRAL KANSAS

By John O. Helgesen[1], Lloyd E. Stullken[2], and A.T. Rutledge[3]

ABSTRACT

Ground-water quality was assessed in a 5,000-square-mile area of the High Plains aquifer in south-central Kansas that is susceptible to nonpoint-source contamination from agricultural and petroleum-production activities. Of particular interest were agricultural chemicals and oil-derived hydrocarbons associated with brines that formerly were disposed of into unlined ponds. Ground-water sampling sites were randomly selected within discrete land-use areas (irrigated cropland, petroleum-production land containing former brine-disposal ponds, and undeveloped rangeland). The sampling design enabled statistical hypothesis testing of the effects of land use, lithology of the unsaturated zone, and type of well sampled.

Results indicate that water beneath irrigated cropland and petroleum-production land is characterized by significantly (95-percent confidence level) larger concentrations of several inorganic constituents than is water beneath undeveloped rangeland. Nondegraded pesticides and oil-derived hydrocarbons were detected only infrequently in the aquifer. The unsaturated zone above the aquifer contains substantial clay that inhibits the downward movement of water and solutes. The type of well sampled (irrigation wells compared to small-yield wells) apparently is not an important factor in the characterization of water quality beneath the irrigated-cropland areas.

INTRODUCTION

As part of the U.S. Geological Survey's Toxic Waste--Ground-Water Contamination Program (Helsel and Ragone, 1984), nonpoint-source contamination of part of the High Plains aquifer in south-central Kansas was assessed. The High Plains aquifer is an extensive, mostly unconfined, heterogeneous sequence of clay, silt, sand, and gravel (Stullken and others, 1985). The study area contains relatively permeable soils and a shallow water table (typically less than 30 feet below land surface); these features make the aquifer particularly susceptible to contamination. The study area is dominated by agricultural land use and also supports petroleum-production activities. Pesticides and oil-derived hydrocarbons--organic contaminants that have the potential to move down to the water table--were of particular interest in this study. The application of pesticides is a common agricultural practice. Brines produced in association with oil likely contain hydrocarbons and formerly were disposed of into unlined ponds.

The objective of this study was to evaluate statistically the occurrence of nonpoint-source contaminants in the High Plains aquifer of south-central Kansas in relation to land use and other factors. This paper presents an overview of the principal results. An initial water-quality reconnaissance of part of the study area is described by Stullken and others (1987). Selected results also have been presented by Helgesen and Thurman (1988), and Helgesen and Rutledge (1989).

STUDY DESIGN

Discrete land-use areas (irrigated cropland, petroleum-production land containing former brine-disposal ponds, and undeveloped rangeland) of 3 to 10 square miles were identified (fig. 1). One small-yield well (generally a domestic or stock well yielding less than 30 gal/min (gallons per minute)) in each discrete area was selected randomly from the wells for which information was available. Sampling and chemical analyses then were done on the assumption that the results would characterize ground-water quality associated with the prevailing overlying land use. The undeveloped rangeland areas, minimally affected by human activities, served as a "control" against which to compare water quality in the developed areas.

In addition to land use, two other factors thought to be pertinent in this regional evaluation were addressed. The effect of unsaturated-zone lithology on ground-water contamination was evaluated by categorizing each land-use area as having either a "clayey" or "sandy" unsaturated zone on the basis of regionalized mapping done as part of this study. Clay within the unsaturated zone possibly inhibits downward movement of water and chemicals. The effect of the type of well sampled was evaluated by also sampling a randomly selected irrigation well (generally yielding more than 500 gal/min) in each irrigated-cropland area. This approach allowed testing of a hypothesis that samples collected from irrigation wells, which draw water from directly beneath fields receiving irrigation water and agricultural chemicals, will contain water with quality different from that of samples from small-yield wells away from the fields. Depths of wells in an area tend to be nearly equal.

The sampling design thus enabled comparisons (fig. 2) on the basis of prevailing land use, lithology of the unsaturated zone (clayey compared to sandy), and type of well sampled (large-yield irrigation compared to small-yield well). Wells were sampled one time, during July 1987. All samples collected were analyzed for major inorganic ions, nutrients, and some other inorganic constituents. Samples from irrigated-cropland areas and from undeveloped rangeland areas also were analyzed for triazine and other nitrogen-containing herbicides and for chlorophenoxy-acid herbicides. Samples from petroleum-production areas and undeveloped rangeland areas were analyzed for

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[3] U.S. Geological Survey, Richmond, Va.

hydrocarbons by gas chromatography with flame-ionization detection (GC-FID scan).

The nonparametric two-tailed Wilcoxon-Mann-Whitney rank-sum test (Iman and Conover, 1983) was used to compare two groups of data to provide a measure of the similarity or dissimilarity of the groups. Contingency-table analysis (Iman and Conover, 1983) helped evaluate data classified by two criteria, such as land use and the presence or absence of a constituent. This approach was appropriate for the organic constituents in this study because they were infrequently detected and, if detected, were present in small concentrations.

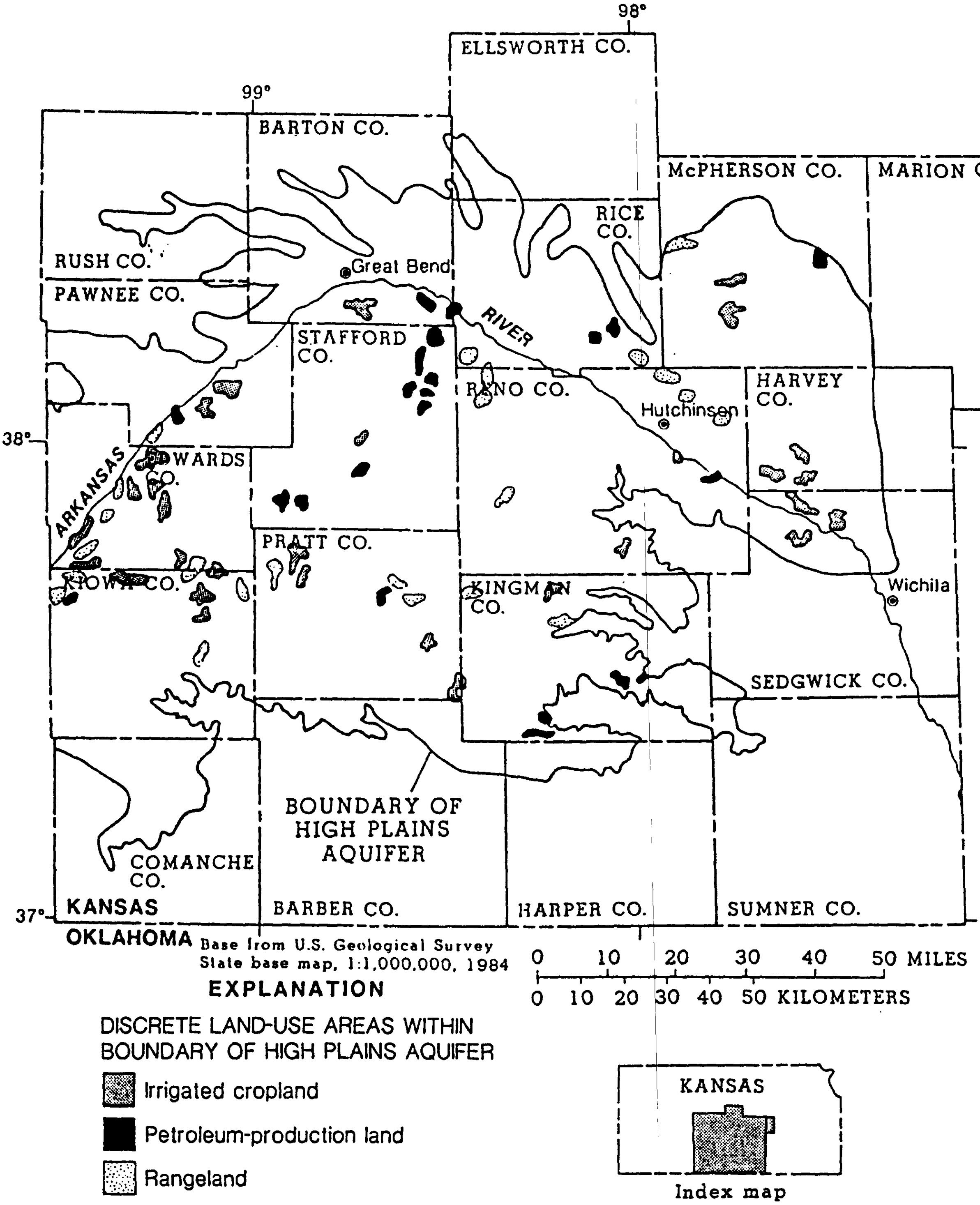
98°
99°
97°
38°
37°
ELLSWORTH CO.
BARTON CO.
McPHERSON CO.
MARION CO.
RICE CO.
RUSH CO.
Great Bend
PAWNEE CO.
RIVER
STAFFORD CO.
RENO CO.
HARVEY CO.
Hutchinson
ARKANSAS
EDWARDS CO.
PRATT CO.
KIOWA CO.
KINGMAN CO.
Wichita
SEDGWICK CO.
BOUNDARY OF HIGH PLAINS AQUIFER
COMANCHE CO.
KANSAS
OKLAHOMA
BARBER CO.
HARPER CO.
SUMNER CO.
Base from U.S. Geological Survey State base map, 1:1,000,000, 1984
0 10 20 30 40 50 MILES
0 10 20 30 40 50 KILOMETERS
EXPLANATION
DISCRETE LAND-USE AREAS WITHIN BOUNDARY OF HIGH PLAINS AQUIFER
▨ Irrigated cropland
■ Petroleum-production land
▨ Rangeland
KANSAS
Index map

Figure 1. Discrete land-use areas delineated as basis for ground-water sampling.

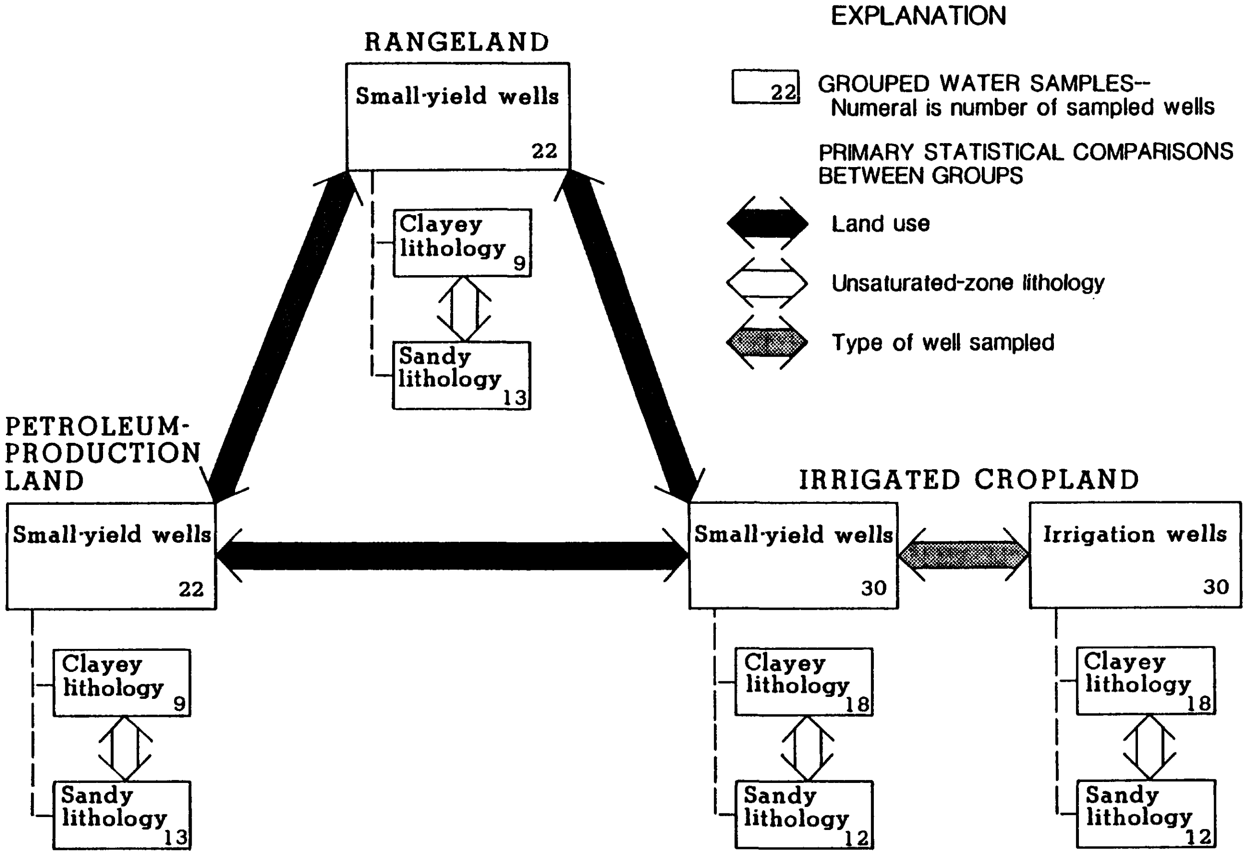
EXPLANATION
22
GROUPED WATER SAMPLES--
Numeral is number of sampled wells
PRIMARY STATISTICAL COMPARISONS BETWEEN GROUPS
Land use
Unsaturated-zone lithology
Type of well sampled
RANGELAND
Small-yield wells
22
Clayey lithology 9
Sandy lithology 13
PETROLEUM-PRODUCTION LAND
Small-yield wells
22
Clayey lithology 9
Sandy lithology 13
IRRIGATED CROPLAND
Small-yield wells
30
Clayey lithology 18
Sandy lithology 12
Irrigation wells
30
Clayey lithology 18
Sandy lithology 12

Figure 2. Groups of water samples for statistical comparisons and number of sampled wells in each group.

Table 1. *Summary of selected water-quality data grouped according to land-use areas*

[Based on data from small-yield wells; units are in milligrams per liter]

	Irrigated cropland (30 samples)			Petroleum-production land (22 samples)			Rangeland (22 samples)		
Property or constituent	Maximum	Minimum	Median	Maximum	Minimum	Median	Maximum	Mini mum	Median
Hardness, total as $CaCO_3$	520	110	180	570	90	190	710	31	130
Alkalinity, as $CaCO_3$	302	40	150	417	77	162	415	28	101
Dissolved solids	900	140	240	1,120	149	335	1,300	88	180
Calcium	160	34	60	180	31	64	140	9.5	44
Magnesium	30	3.2	7.1	35	2.5	6.6	88	1.8	4.0
Sodium	100	5.8	23	200	8.5	32	440	6.8	13
Potassium	5	1	3	9	1	2	6	.9	2
Sulfate	440	7.8	22	150	9.1	16	380	10	15
Chloride	140	2.9	14	460	3.2	50	620	2.7	7.9
Nitrite plus nitrate	18	.1	6.8	23	.46	3.6	36	1.1	3.4
Orthophosphorus	.13	.01	.05	.14	.01	.06	.49	.01	.07

RESULTS

Relation of Water Quality to Land Use

Some of the water-quality data are summarized in table 1. The rank-sum test was used to compare each pair of the three land-use areas, in terms of median values of properties (pH, water temperature, hardness, and alkalinity) and median inorganic-constituent concentrations. The results are illustrated by plots of test confidence levels that exceed 80 percent (fig. 3). For several properties or constituents, these confidence levels equaled or exceeded 95 percent--a level of confidence that is used in this paper to define statistically significant differences between groups. At a 95-percent confidence level, concentrations of hardness, alkalinity, calcium, magnesium, potassium, fluoride, and nitrite plus nitrate are significantly larger in irrigated-cropland areas than in rangeland areas. pH and concentrations of hardness, alkalinity, dissolved solids, sodium, and chloride are significantly larger in petroleum-production areas than in rangeland areas. Water-quality comparisons between irrigated cropland and petroleum-production land indicated few significant differences; relatively large nitrite-plus-nitrate concentrations are associated with irrigated cropland.

Pesticide-detection results are summarized in table 2. The contingency-table test was used to compare the frequency of atrazine detection beneath irrigated cropland (4 out of 30 samples from small-yield wells) to the frequency of detection beneath rangeland (1 out of 22 samples). The test indicated a confidence level of 71 percent--a level that did not demonstrate a significant association between atrazine occurrence and land use. However, the small numbers of detections may have lessened the reliability of the results.

The relation of hydrocarbons in ground water to land use was evaluated in terms of total concentrations of organic compounds as estimated from GC-FID chromatograms. Boxplots (fig. 4) illustrate very similar distributions between total concentrations of organic compounds in samples from petroleum-production areas and samples from rangeland areas. The rank-sum test indicated that the confidence level was 84 percent--a level that did not demonstrate a significant difference.

Relation of Water Quality to Unsaturated-Zone Lithology

Because each land-use area is located within a regionally delineated area of either "clayey" or "sandy" unsaturated-zone lithology, samples from each land-use area were grouped further on this basis. The effect of this factor was assessed by repeating comparisons between land-use areas separately for the clayey- and sandy-lithology data. Results of rank-sum tests that were applied only to the data from clayey unsaturated-zone areas indicated few significant differences between land-use areas. However, most of the previously noted significant differences (before subdividing by lithology) remained significant when tests were applied to the data from the sandy unsaturated-zone areas.

Tests of frequency of atrazine detection and of total organic-compound concentration were repeated according to unsaturated-zone lithology. Comparisons indicated no significant associations between the occurrence of these constituents and the lithology.

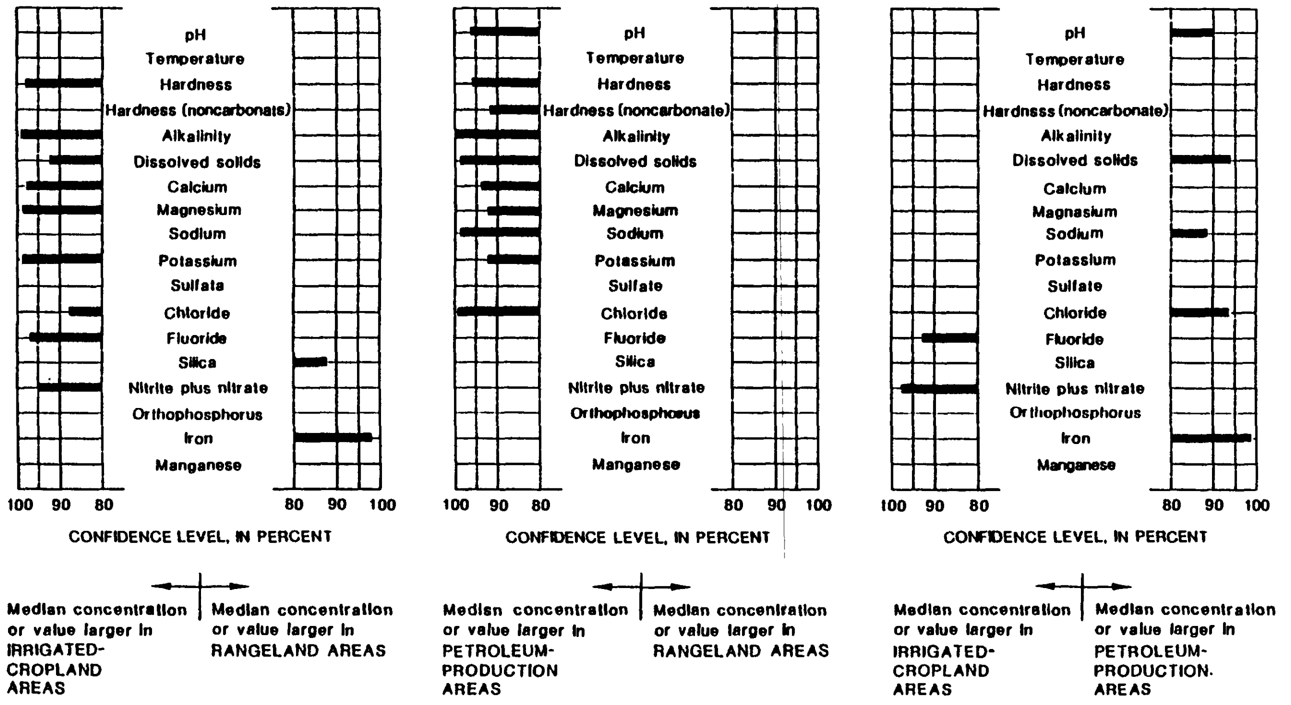

Figure 3. Confidence levels of differences between median property values or inorganic-constituent concentrations in water samples from small-yield wells in different land-use areas, based on two-tailed Wilcoxon-Mann-Whitney rank-sum tests.

Table 2. *Frequency of detections of pesticides in ground-water samples grouped according to land-use areas, unsaturated-zone lithology, and type of well sampled*

Land-use area (type of well sampled)	Number of samples	Constituent						
		Alachlor	Atrazine	Metolachlor	Propazine	Trifluralin	2,4-D	Other triazine and chlorophenoxy-acid herbicides
All data								
Irrigated cropland								
(small-yield wells)	30	0	4	0	1	1	1	0
(irrigation wells)	30	1	3	2	1	1	0	0
Rangeland	22	0	1	0	0	0	0	0
Clayey unsaturated-zone lithology								
Irrigated cropland								
(small-yield wells)	18	0	1	0	1	0	1	0
(irrigation wells)	18	0	2	1	1	1	0	0
Rangeland	9	0	1	0	0	0	0	0
Sandy unsaturated-zone lithology								
Irrigated cropland								
(small-yield wells)	12	0	3	0	0	1	0	0
(irrigation wells)	12	1	1	1	0	0	0	0
Rangeland	13	0	0	0	0	0	0	0

Relation of Water Quality to Type of Well Sampled

Testing for differences in ground-water quality according to type of well sampled was limited to the irrigated-cropland areas. On the basis of rank-sum tests, significant differences were not indicated for any major ions and most other constituents.

The contingency-table test was used to compare the frequency of atrazine detection in samples from small-yield wells to that in samples from irrigation wells. The test indicated that the confidence level was 69 percent--a level that did not demonstrate a significant association between atrazine occurrence and type of well sampled; again, small numbers of detections may have lessened the reliability of the results.

DISCUSSION

The relatively large concentrations of several constituents in ground water beneath irrigated-cropland areas, as compared to undeveloped rangeland areas, probably result from infiltration and percolation of water through the tilled soil and the unsaturated zone, a large part of which consists of applied irrigation water that has been concentrated by evapotranspiration. The water dissolves minerals from the soil and subsoil as well as chemicals applied as fertilizer, which then are transported down to the aquifer (Helgesen and Rutledge, 1989).

The relatively large concentrations of several constituents in ground water beneath petroleum-production lands probably reflect the downward percolation of brines from leaky disposal ponds in those areas. Detections of trace-organic compounds were similar in petroleum-production lands and undeveloped rangelands, indicating that most or all of these organic compounds are natural in origin and probably derived from dissolution from soil or aquifer materials.

The unsaturated zone is lithologically heterogeneous and contains substantial clay that inhibits the downward movement of water and solutes (Helgesen and Rutledge, 1989). Degradation and sorption probably account for infrequent detection of atrazine in the ground water (Helgesen and Rutledge, 1989; Rutledge and Helgesen, 1990).

The lack of association between water quality and type of well sampled suggests that the type of well sampled is not important in characterizing water quality beneath the irrigated-cropland areas. That is, the pumping of irrigation wells does not appear to divert enough regional flow to cause local anomalies of mineralized ground water.

CONCLUSIONS

Results of this study indicate that regional water quality of the High Plains aquifer in south-central Kansas has been affected by prevailing land-use activities. The effects are principally in the form of increased concentrations of inorganic, rather than organic, constituents.

Ground water beneath irrigated-cropland areas is characterized by significantly larger concentrations of hardness, alkalinity, calcium, magnesium, potassium, fluoride, and nitrite plus nitrate than water beneath undeveloped rangeland. Nondegraded pesticides were detected infrequently in the aquifer. Atrazine was the most commonly detected pesticide but appeared to be present only locally in the ground water beneath irrigated-cropland areas; this scarcity probably results from degradation and sorption.

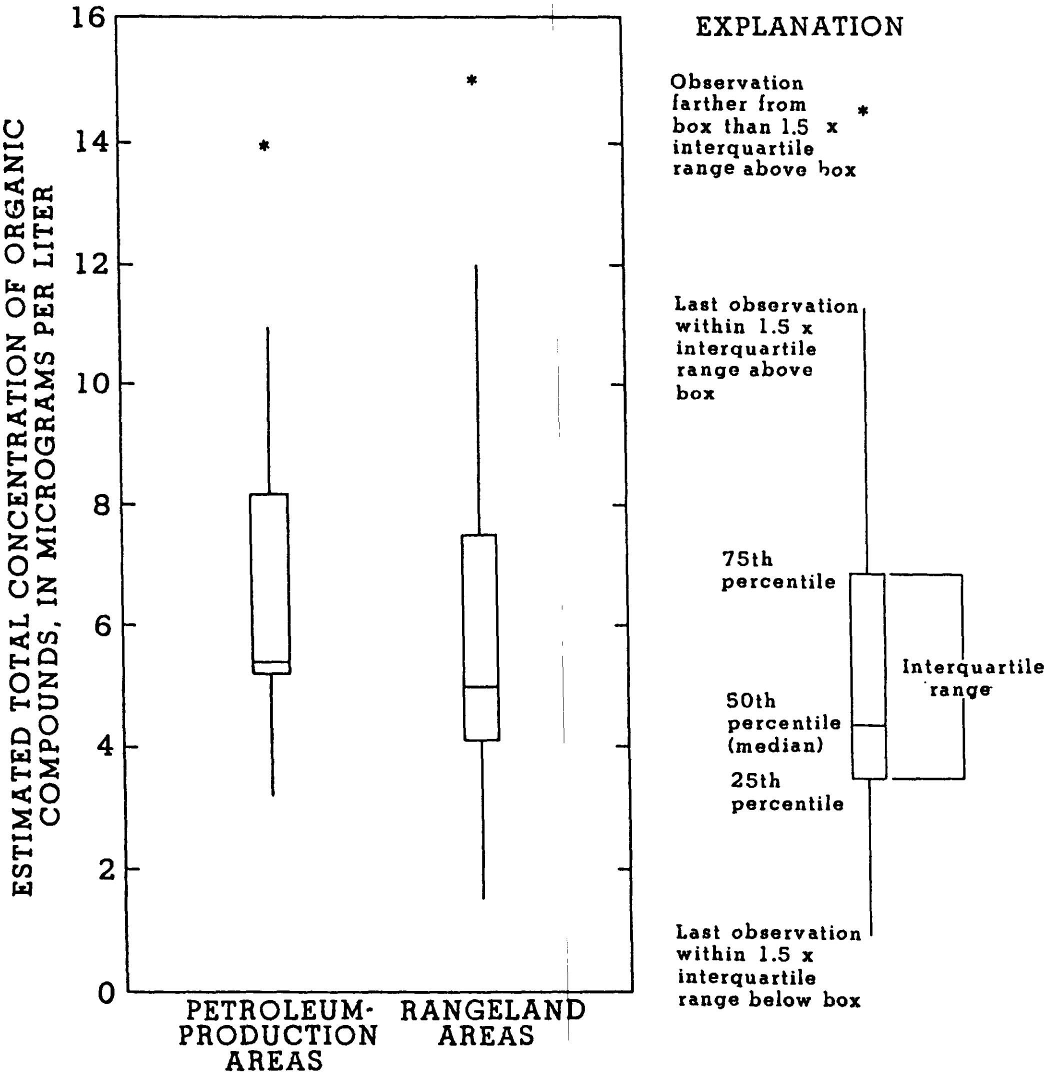

Figure 4. Estimated total concentrations of organic compounds in ground-water samples from petroleum-production and rangeland areas (based on 22 petroleum-production-area samples and 23 rangeland-area samples; one additional rangeland sample was analyzed by gas chromatography with flame-ionization detection, as compared with analyses for inorganic constituents and pesticides).

Ground-water quality beneath petroleum-production lands containing former brine-disposal ponds exhibited significantly higher pH and larger concentrations of hardness, alkalinity, dissolved solids, sodium, and chloride than water beneath undeveloped rangeland. Nonpoint-source contamination by oil-derived hydrocarbons was not discernible.

Results describing relations between ground-water quality and unsaturated-zone lithology were mixed; the unsaturated zone contains substantial clay that inhibits the downward movement of water and solutes. Lack of association between water quality and type of well sampled suggests that diversion of regional flow by the pumping of irrigation wells does not affect significantly the characterizing of water quality beneath the irrigated-cropland areas.

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COMPARISON OF RELATIONS BETWEEN SHALLOW GROUND-WATER QUALITY AND LAND USE IN TWO NEW JERSEY COASTAL PLAIN AQUIFER SYSTEMS

By Eric F. Vowinkel[1]

ABSTRACT

Relations between shallow-ground-water quality and land use were tested statistically by analysis of data from wells located within the outcrop areas of two aquifer systems in the New Jersey Coastal Plain. Water samples from wells in undeveloped, agricultural, residential, and urban-nonresidential areas were analyzed for nitrate and purgeable organic compounds. Water samples from wells in agricultural areas were analyzed for five pesticide groups: organochlorine, organophosphorous, carbamate, triazine/acetanilide, and chlorophenoxy acid.

In both aquifer systems, relations between these constituents and land use were similar. Concentrations of nitrate in ground water beneath agricultural land were significantly higher than those in ground water underlying other land-use areas. Purgeable organic compounds were detected less frequently in ground water beneath agricultural land than in ground water underlying urban or undeveloped land. The detection frequency of each pesticide group was similar for both aquifer systems; carbamate insecticides were detected most frequently.

INTRODUCTION

As part of a project investigating nonpoint-source ground-water contamination in the New Jersey Coastal Plain, methods were developed and tested to determine whether statistically significant relations exist between shallow ground-water quality and land use. This paper compares these statistical relations for two aquifer systems as a test of the transfer value of the methods used and results obtained to other areas with similar hydrogeologic conditions, climate, and land use. Concentrations of nitrate plus nitrite as nitrogen, purgeable organic compounds, and pesticides in ground water appear to be related to land use.

The New Jersey Coastal Plain, which comprises about 10,900 km^2 (square kilometers) in southern New Jersey (fig. 1), is underlain by a seaward-dipping wedge of unconsolidated sediments consisting of alternating layers of sand, silt, and clay of Cretaceous to Holocene age (fig. 2). The hydrogeologic framework of (Zapecza, 1989) and regional ground-water flow in (Martin, 1990) the New Jersey Coastal Plain are well documented. Two major aquifers, the Potomac-Raritan-Magothy aquifer system (Aquifer 1) and the Kirkwood-Cohansey aquifer system (Aquifer 2), supply more than 90 percent of the freshwater used by the more than 3 million people living in the New Jersey Coastal Plain. Aquifer 1 underlies the entire Coastal Plain but crops out in a narrow 5- to 16-km-wide strip of land that comprises about 1,000 km^2 of land extending from Raritan Bay to Delaware Bay. The outcrop area of Aquifer 2 exceeds 7,500 km^2.

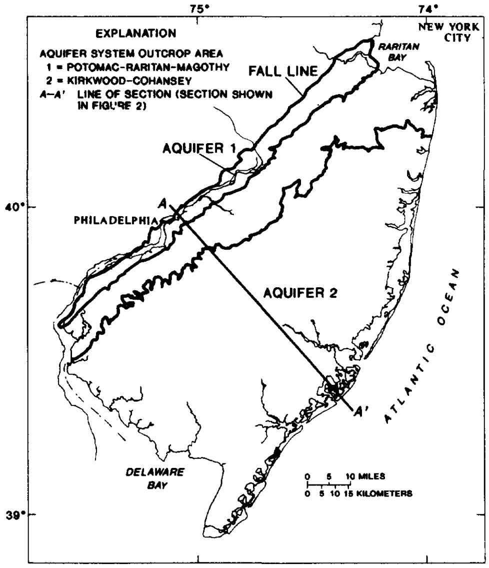
75°
74°
EXPLANATION
AQUIFER SYSTEM OUTCROP AREA
1 = POTOMAC-RARITAN-MAGOTHY
2 = KIRKWOOD-COHANSEY
A–A' LINE OF SECTION (SECTION SHOWN IN FIGURE 2)
FALL LINE
NEW YORK CITY
RARITAN BAY
AQUIFER 1
A
40°
PHILADELPHIA
AQUIFER 2
ATLANTIC OCEAN
A'
DELAWARE BAY
0 5 10 MILES
0 5 10 15 KILOMETERS
39°

Figure 1. Location of the study areas and line of generalized hydrogeologic section.

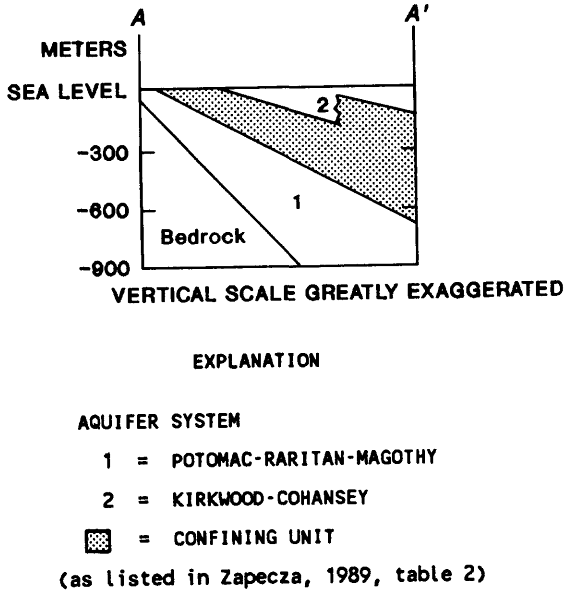
A
A'
METERS
SEA LEVEL
-300
-600
-900
2
1
Bedrock
VERTICAL SCALE GREATLY EXAGGERATED
EXPLANATION
AQUIFER SYSTEM
1 = POTOMAC-RARITAN-MAGOTHY
2 = KIRKWOOD-COHANSEY
▨ = CONFINING UNIT
(as listed in Zapecza, 1989, table 2)

Figure 2. Generalized hydrogeologic section through the New Jersey Coastal Plain.

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[1] U.S. Geological Survey, West Trenton, N.J.

The outcrop areas of both aquifer systems contain a variety of land uses (fig. 3). About 30 percent of the outcrop area of Aquifer 1 consists of undeveloped land (forest land, wetlands, and barren land), compared to about 70 percent for Aquifer 2. Agricultural land comprises nearly 20 percent of both outcrop areas. Urban land was divided into two categories--residential and nonresidential. The percentages of residential and nonresidential land overlying the outcrop area of Aquifer 1 are greater than the percentages for Aquifer 2 because most of the outcrop area of Aquifer 1 is located within the urban corridor between New York City and Philadelphia.

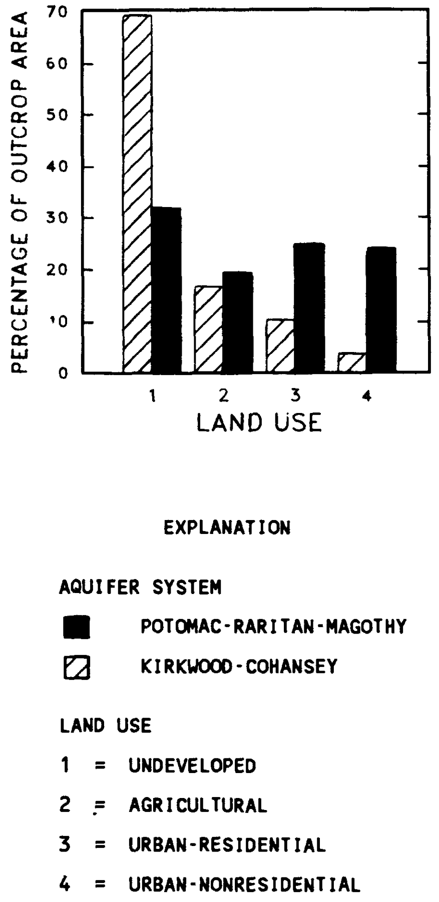


Figure 3. Percentages of the four predominant land-use groups in each outcrop area.

DATA-BASE DEVELOPMENT AND METHODS

Information on well locations, well-construction characteristics, water quality, hydrogeologic conditions, and land use were collected and stored in a geographic information system (GIS). Ground-water-quality data used in this statistical analysis were obtained from samples collected during 1980-90 and analyzed at the U.S. Geological Survey National Water-Quality Laboratory or at the New Jersey District laboratory in Trenton, N.J. Well-selection criteria were established to reduce sampling biases associated with hydrogeologic conditions, well-construction characteristics, and spatial autocorrelation (Vowinkel and Battaglin, 1989a; Barringer and others, 1990). Only wells located within the outcrop areas with depths equal to or less than 30.5 m (meters) below land surface were included.

Percentages of undeveloped, agricultural, residential, and urban-nonresidential land within 400- and 800-m-radius circular buffer zones centered on the wellhead were calculated from digital land-use and land-cover data obtained from the National Cartographic Information Center (Anderson and others, 1976; Fegeas and others, 1983). The buffer zones were used to quantify the land area surrounding a well that potentially could affect water quality.

The effect of the spatial sampling density of wells on the results was evaluated by considering minimum well-separation distances of 0, 400, 800, 1,200, 1,600, and 2,000 m. Water- quality observations from sites located near each other can be spatially autocorrelated and lack independence. Also, some land uses are counted more than once where buffer zones overlap. A GIS program was developed to generate subsamples that maximizes the number of wells remaining while meeting the minimum well-separation-distance criterion.

Three methods of quantifying the relation between ground-water quality and land use were developed: the predominant land-use method, the present/absent land-use method, and the land-use percentage method (Vowinkel and Battaglin, 1989b). The predominant- and present/absent land-use methods are emphasized in this report. Nonparametric statistical methods were used to test for differences in constituent concentrations in ground water among the four land-use groups. The Kruskal-Wallis (K-W) test was used to determine whether one or more of the groups is different. The Mann-Whitney (M-W) test was used to compare concentrations among the land-use groups. The Chi-square test was used to compare frequencies of detection of a constituent among land-use groups. If the test statistic meets or exceeds a 0.05 significance level, then one or more of the groups is considered significantly different.

RELATION BETWEEN GROUND-WATER QUALITY AND LAND USE

Nitrates

Natural sources of nitrate in ground water in undeveloped areas are limited, although nitrate can be imported from agricultural or urban land through atmospheric deposition or ground-water flow. In agricultural areas, sources of nitrate to ground water include septic systems, crop fertilizers, and manure from stock and poultry farms. Sources of nitrate to ground water in urban areas include septic systems, leaky sewer pipes, lawn fertilizers, and industrial wastes. Nitrate concentrations were expected to be lowest in ground water beneath undeveloped land and highest beneath agricultural land.

Concentrations of dissolved nitrate as nitrogen were separated into four sets on the basis of the four predominant land-use groups. K-W test statistics were calculated for two buffer-zone sizes and for six minimum well-separation distances (fig. 4). In all cases, the test statistic exceeded a significance level of 0.05, which indicates that the distribution of nitrate concentrations in ground water underlying one or more of the land-use groups is significantly different from that beneath the others. In all cases, the K-W test statistic is greatest at a minimum well-separation distance of 0 m and decreases as this distance increases. The K-W test statistics tend to level off at a minimum well-separation distance of 1,200 m and greater. This result reflects the effect of spatial autocorrelation at well-separation distances less than 1,200 m.

In all cases, the buffer-zone size has a minor effect on the relation between nitrate concentration and land use; the lines connecting the K-W test statistics are parallel (fig. 4). The statistical relation is stronger for Aquifer 2 than for Aquifer 1. For Aquifer 1, the test statistic is greatest for the 800-m buffer zone, whereas for Aquifer 2 it is greatest for the 400-m buffer zone. These differences between results for Aquifer 1 and Aquifer 2 probably reflect the greater frequency of multiple land uses within the buffer zones of wells in Aquifer 1 compared to those of wells in Aquifer 2.

The relation between nitrate (as N) and land use for each aquifer system was tested by using data sets with a minimum well-separation distance of 1,600 m and land uses within the 800-m buffer zone (fig. 5).

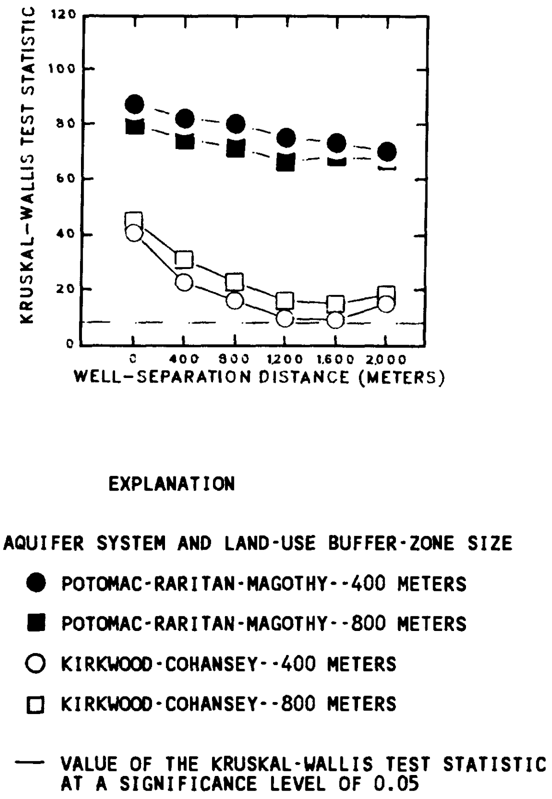


Figure 4. Effect of buffer-zone size and minimum well-separation distance on the relation between nitrate concentration and land use for the four predominant land-use groups.

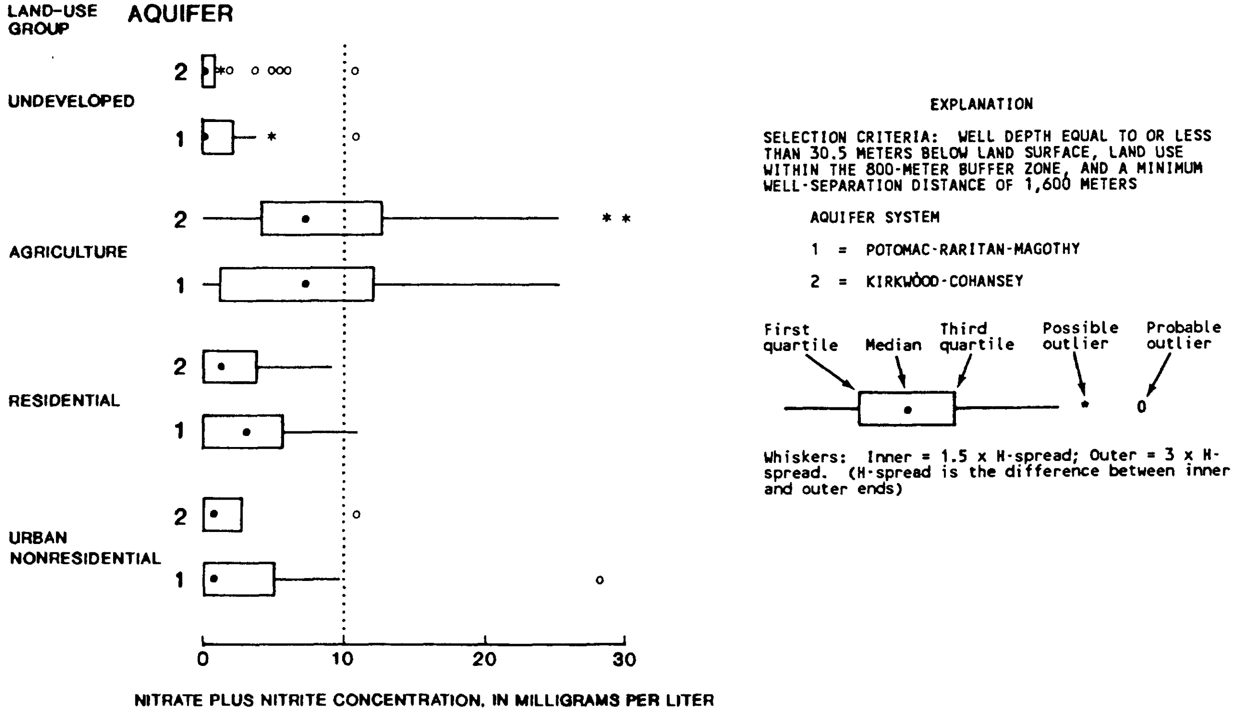


Figure 5. Distribution of concentrations of nitrate as nitrogen in water from wells, by predominant land-use group.

Nitrate concentrations were similar within each of the four land-use groups; however, differences were found among the land-use groups. Nitrate concentrations in ground water in undeveloped areas were lower than those in the other land-use areas; the median nitrate (as N) concentration in undeveloped areas was less than 0.1 mg/L (milligram per liter) for both aquifer systems. Nitrate concentrations in ground water in agricultural areas are higher than those in the other land-use areas; the median nitrate (as N) concentration in ground water from agricultural land exceeded 7 mg/L, and concentrations at more than 25 percent of the sites exceeded 10 mg/L in both aquifers. Nitrate (as N) concentrations in ground water from residential and nonresidential areas were similar and rarely exceeded 10 mg/L.

Purgeable Organic Compounds

Purgeable organic compounds (POCs) include aliphatic and aromatic organic compounds. Trichloroethene, tetrachloroethene, and 1,1,1-trichloroethane are chlorinated aliphatic compounds that commonly are used as industrial and household solvents. Benzene and toluene are aromatic compounds that are components of gasoline, oil, and heating fuels. Water samples collected from 169 wells screened in Aquifer 1 and 67 wells screened in Aquifer 2 were analyzed for POCs. The 11 POCs included in this analysis were combined into one group to test the relation between POCs and land use (table 1). POCs were expected to be detected most frequently in ground water beneath urban land and least frequently in ground water beneath undeveloped land.

The POC detection frequency was higher in Aquifer 1 than in Aquifer 2 (table 1) because the outcrop area of Aquifer 1 contains a higher percentage of urban land. The detection frequency depends on the minimum well-separation distance. In Aquifer 1, the POC detection frequency was about 28 percent at a minimum well-separation distance of 0 m; however, the detection frequency was about 20 percent or less at distances of 400 m and greater. The higher POC detection frequency at a well-separation distance of 0 m is partly a result of the spatial autocorrelation of some water-quality observations. The POC detection frequency in Aquifer 2 was about 12 to 13 percent at all well-separation distances because few wells in Aquifer 2 are clustered.

The K-W test was used to test for differences in POC concentrations among three predominant land-use groups--undeveloped, agricultural, and urban (fig. 6). The number of available samples from the urban-nonresidential group in Aquifer 2 was insufficient to compute valid test statistics for all four land-use groups. The results of the analysis indicate that buffer-zone size affects the test statistics for Aquifer 1. The K-W test statistics are not significant for either buffer-zone size at well-separation distances of 1,600 and 2,000 m for Aquifer 1, possibly because these contaminants mostly are derived from point sources.

Table 1. *Detection frequency of purgeable organic compounds at concentrations equal to or exceeding 3 micrograms per liter in water from wells with depths equal to or less than 30.5 meters below land surface*

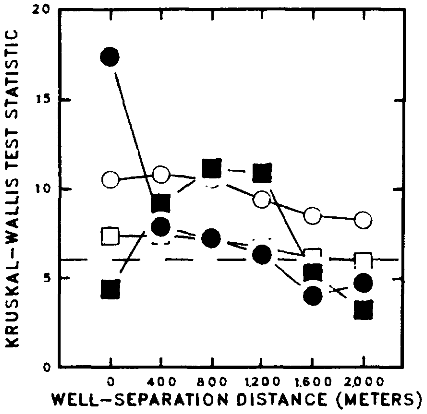
	Number of detections											
	Aquifer 1						Aquifer 2					
	Well-separation distance (meters)						Well-separation distance (meters)					
Purgeable organic compound (POC)	0	400	800	1,200	1,600	2,000	0	400	800	1,200	1,600	2,000
Benzene	25	8	7	4	2	2	5	5	5	5	5	5
Carbon tetrachloride	4	0	0	0	0	0	0	0	0	0	0	0
Chloroform	13	3	2	2	2	3	2	2	2	2	1	1
Methylene chloride	15	5	5	2	1	2	1	1	1	1	1	1
Tetrachloroethylene	18	7	6	3	2	3	1	1	1	1	1	1
Toluene	22	5	4	3	1	1	2	2	2	2	2	2
Trichloroethylene	24	8	7	5	3	4	2	2	2	2	2	2
1,1-Dichloroethane	11	2	2	0	0	0	0	0	0	0	0	0
1,1,1-Trichloroethane	12	5	4	3	2	3	1	1	1	1	1	1
1,2-Dichloroethane	19	5	3	2	1	2	0	0	0	0	0	0
Vinyl chloride	19	4	3	1	1	2	0	0	0	0	0	0
Any POC detected	47	22	19	15	8	11	8	8	8	8	7	7
Total wells sampled	169	110	93	77	63	54	67	65	64	60	57	56
Percentage detected	27.8	20.0	20.4	19.4	12.7	20.4	11.9	12.3	12.5	13.3	12.3	12.5

The relation between POC concentration and predominant land-use group in each aquifer was compared by using wells with a minimum well-separation distance of 800 m and land uses within the 400-m buffer zone (fig. 7). POC concentrations and detection frequencies were significantly lower in ground water beneath agricultural land than in ground water underlying undeveloped and urban areas for both aquifer systems. No difference in POC concentrations between the urban and undeveloped land-use groups was observed for either aquifer system. The POC detection frequency in ground water beneath undeveloped land was higher than expected, possibly because of improper disposal of POCs in undeveloped areas near urban land. Urban land is present within the 400-m buffer zone of all 19 wells screened in Aquifer 1 at which POCs were detected. Urban land is present within the 400-m buffer zone of five of the eight wells screened in Aquifer 2 at which POCs were detected; urban land is present within the 800-m buffer zone of all but one of the eight wells.

Pesticides

Water samples collected during the summer months of 1986 and 1987 from 81 wells screened in sediments in Aquifer 1 or Aquifer 2, and located in agricultural areas where pesticides are used, were analyzed for five pesticide groups: organochlorine, organophosphorous, carbamate, triazine/acetanilide, and chlorophenoxy acid (Louis and Vowinkel, 1989). Well depths ranged from 5 to 50 m. Pesticide residues were detected in water from 27 of the 81 wells; 16 pesticides and 3 pesticide metabolites were detected in concentrations ranging from 0.01 to 13 micrograms per liter (table 2). Each sample was not analyzed for all five pesticide groups because analytical methods were not available at the time of sampling or because sample bottles were mishandled between the field and laboratory.

The detection frequency of one or more pesticides in each of the five groups in both aquifer systems (fig. 8) was compared by using wells selected on the basis of the following criteria: presence of agricultural land within the 800-m buffer zone, maximum depth of 35.5 m below land surface, and minimum well-separation distance of 1,600 m.



EXPLANATION

AQUIFER SYSTEM AND BUFFER-ZONE SIZE

● POTOMAC-RARITAN-MAGOTHY--400 METERS

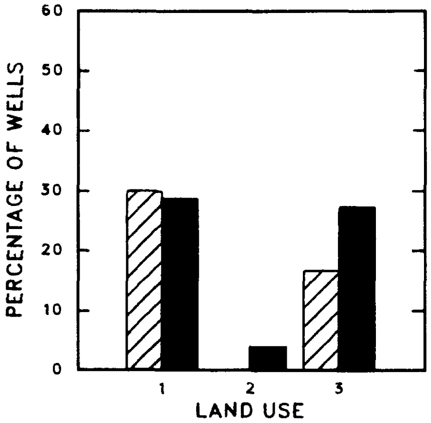
■ POTOMAC-RARITAN-MAGOTHY--800 METERS

○ KIRKWOOD-COHANSEY--400 METERS

□ KIRKWOOD-COHANSEY--800 METERS

— — VALUE OF THE KRUSKAL-WALLIS TEST STATISTIC AT A SIGNIFICANCE LEVEL OF 0.05

Figure 6. Effect of buffer-zone size and minimum well-separation distance on the relation between concentration of purgeable organic compounds and predominant land-use group.



EXPLANATION

SELECTION CRITERIA: DETECTION LEVEL OF PURGEABLE ORGANIC COMPOUNDS EQUAL TO 3 MICROGRAMS PER LITER, WELL DEPTH EQUAL TO OR LESS THAN 30.5 METERS BELOW LAND SURFACE, LAND USE WITHIN THE 400-METER BUFFER ZONE, AND A MINIMUM WELL-SEPARATION DISTANCE OF 800 METERS.

AQUIFER SYSTEM

■ POTOMAC-RARITAN-MAGOTHY

▨ KIRKWOOD-COHANSEY

LAND USE

1 = UNDEVELOPED
2 = AGRICULTURAL
3 = URBAN (RESIDENTIAL AND NONRESIDENTIAL)

Figure 7. Detection frequency of purgeable organic compounds in ground water, by predominant land-use group.

Table 2. *Pesticide residues detected in water from wells in agricultural areas of the New Jersey Coastal Plain*[1] *(Modified from Louis and Vowinkel, 1989)*

Pesticide	Number of wells sampled	Number of times detected	Range of concentrations (micrograms per liter)
Insecticides			
Organochlorine			
DDD	80	2	0.02
DDT	80	1	.02
Dieldrin	80	5	.03 - 0.04
Endosulfan	50	2	.01
Endrin	80	1	.01
Lindane	80	2	.08 - 0.14
Methoxyclor	80	1	.05
Organophosphorous			
Diazinon	79	1	.01
Carbamate			
Aldicarb sulfone	51	9	1.1 - 4.4
Aldicarb sulfoxide	51	7	.7 - 5.3
Carbofuran	51	8	.5 - 6.6
Methomyl	51	4	.5 - 1.0
Oxamyl	51	1	1.4
Herbicides			
Triazine/acetanilide			
Atrazine	80	7	.1 - 0.8
Metribuzin	80	2	.1
Prometon	80	4	.1 - 0.3
Simazine	80	4	.1 - 0.3
Alachlor	49	5	.1 - 13.0
Metolachlor	49	2	.1
Chlorophenoxy acid (none detected)			

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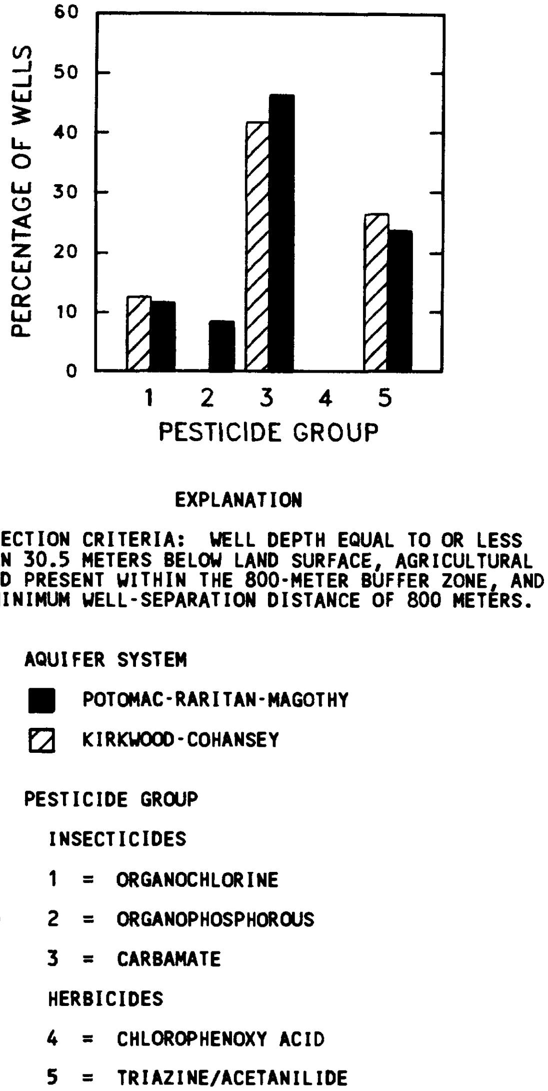
[1] A total of 81 wells were sampled and analyzed for one or more of five pesticide groups, however, analytical results are not reported for all five groups for each well because analytical methods were not available or sample bottles were mishandled between the field and laboratory.

The frequency of detection of pesticides for each pesticide group is similar for both aquifer systems. No chlorophenoxy acid herbicides were detected. Diazinon was the only organophosphorous insecticide detected. Organochlorine compounds were detected in water from about 10 percent of the wells in both aquifer systems; dieldrin was detected most frequently. Carbamate insecticides were detected in more than 40 percent of the samples from each of the aquifer systems; carbofuran and the metabolites of aldicarb were detected most frequently. Triazine/acetanilide herbicides were detected in more than 20 percent of the samples in each of the aquifer systems; atrazine and alachlor were detected most frequently.

SUMMARY

The relations between shallow ground-water quality and land use are statistically similar for two New Jersey Coastal Plain aquifer systems; the Potomac-Raritan-Magothy aquifer system and the Kirkwood-Cohansey aquifer system. Concentrations of nitrate in water from wells in agricultural areas were significantly higher than those in water from wells in residential, urban-nonresidential, and undeveloped land areas in both aquifer systems. POCs were detected less frequently in ground water beneath agricultural land than in ground water underlying urban or undeveloped land. The types and frequency of detection of pesticide residues in water from wells in agricultural areas were similar for both aquifer systems. These results indicate that the methods applied in this study and the results of the statistical analyses of the relations between water quality and land use probably are transferable to other areas with similar hydrogeology, climate, and land use.



SELECTION CRITERIA: WELL DEPTH EQUAL TO OR LESS THAN 30.5 METERS BELOW LAND SURFACE, AGRICULTURAL LAND PRESENT WITHIN THE 800-METER BUFFER ZONE, AND A MINIMUM WELL-SEPARATION DISTANCE OF 800 METERS.

Figure 8. Frequency of detection of five pesticide groups in water from wells in agricultural areas, by aquifer.

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DISTRIBUTION OF DISSOLVED ATRAZINE AND TWO METABOLITES IN THE UNCONFINED AQUIFER, SOUTHEASTERN DELAWARE

By Judith M. Denver[1] and Mark W. Sandstrom[2]

ABSTRACT

Water from 20 shallow wells in a mostly agricultural watershed in southeastern Delaware was analyzed for atrazine and two of its metabolites, desethylatrazine and deisopropylatrazine, along with nitrate and silica. Atrazine or its metabolites were present in all the water samples and ranged in concentration from a trace to 2,830 nanograms per liter. Desethylatrazine was the predominant metabolite and in most wells was present in higher concentrations than atrazine. High concentrations of atrazine and metabolites are associated with high concentrations of nitrate. The ratio of desethylatrazine to total atrazine increased from less than 0.1 to from 0.8 to 1.0 along a ground-water flow path originating in an agricultural area. Changes in concentration and relative proportions of atrazine and the metabolites along the flow path might be caused by continued microbial degradation in the ground water, although other processes, such as dilution and changes in aquifer recharge rate, also could be important.

INTRODUCTION

Atrazine is an s-triazine herbicide used primarily for control of broadleaf and grassy weeds in corn and soybean cultivation. It is the second most widely used herbicide in the United States. This factor, together with its relatively high solubility in water, low tendency to sorb to soil organic matter, and persistence in soil explains why atrazine has been detected in ground water more frequently than any other herbicide (Hallberg, 1989; Leistra and Boesten, 1989).

Atrazine is degraded in the soil zone by microorganisms. Several of the metabolites, such as hydroxyatrazine and s-glutathione atrazine, are strongly sorbed by soils and, thus, are less likely to reach to ground water than atrazine (Clay and Koskinen, 1990). The metabolites that result from removal of an alkyl side chain, desethylatrazine (DEA) and deisopropylatrazine (DIA), have physical and chemical properties similar to that of atrazine, and so would be expected to migrate with atrazine to ground water. Once a pesticide enters the ground-water system, degradation, adsorption, or dilution may continue, although little is known about these processes in ground water.

This study is adjunct to a larger study of the distribution of agricultural chemicals in the unconfined aquifer in southeastern Delaware (Denver, 1989). The purpose of the work presented here is to examine the distribution of atrazine, its metabolites DEA and DIA, and nitrate in ground water. This paper presents analyses of atrazine and its metabolites DEA and DIA, silica, and nitrate in 20 water samples from the unconfined aquifer. Water samples were collected along a flow path that originates in an area with agricultural land use to study the presence of atrazine and its relation to its metabolites. The data-collection program was designed to obtain representative samples along a flow path of increasingly older and deeper water.

Study Area

The study area is in the Coastal Plain of eastern Sussex County, Del. (fig. 1). Land uses are predominantly agricultural (corn and soybean production) and forest. Aerial photographs show that land use has been relatively constant since the late 1930's. Soils are generally well-drained sandy loams. The area receives average annual precipitation of 44 in. (inches) of which approximately 14 in. directly recharges the unconfined aquifer. Most recharge occurs from mid-October to early April when evapotranspiration is at a minimum (Johnston, 1973). The water-table depth ranges from less than 1 to 19 ft (feet) below the land surface; annual water-table fluctuation ranges from 3 to 10 ft. Ground-water flow is predominantly from west to east across the study area. The unconfined aquifer, which is about 100 ft thick, consists mainly of permeable quartz sand and gravel; it is susceptible to contamination by nitrate and other chemical constituents associated with agricultural practices. Atrazine has been applied to crops in this area for more than 30 years. Detailed information on ground-water flow, water chemistry, and the observation-well network is given in Denver (1989).

Sampling Methods

The locations of wells sampled in winter 1989-90 are shown in figure 1. The wells are arranged in clusters and are screened at different depths in the aquifer. A hydrogeologic section showing the configuration of the clusters and the wells selected to represent the ground-water flow path is also shown in figure 1. Water samples were collected in December 1989 and January 1990, about 9 months after the normal early spring herbicide application, using a submersible Teflon[3]-gear impeller pump connected to Teflon tubing. Equipment was thoroughly cleaned with laboratory detergent prior to sampling and rinsed in the field with distilled water between sites. No herbicides were detected in field equipment blanks periodically collected during the study. All herbicide samples were collected in 1-liter amber glass bottles and shipped on ice to the laboratory, where they were refrigerated at 4°C (degrees Celsius) for up to a maximum of 5 days prior to processing. Treatment and processing of silica and nitrate samples followed methods given in Fishman and Friedman (1989). Atrazine and metabolites were determined by the solid-phase extraction and gas chromatography/mass spectrometry method described by Sandstrom (1989).

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[3] The use of trade names in this paper is for identification purposes only and does not constitute endorsement by the U.S.Geological Survey.

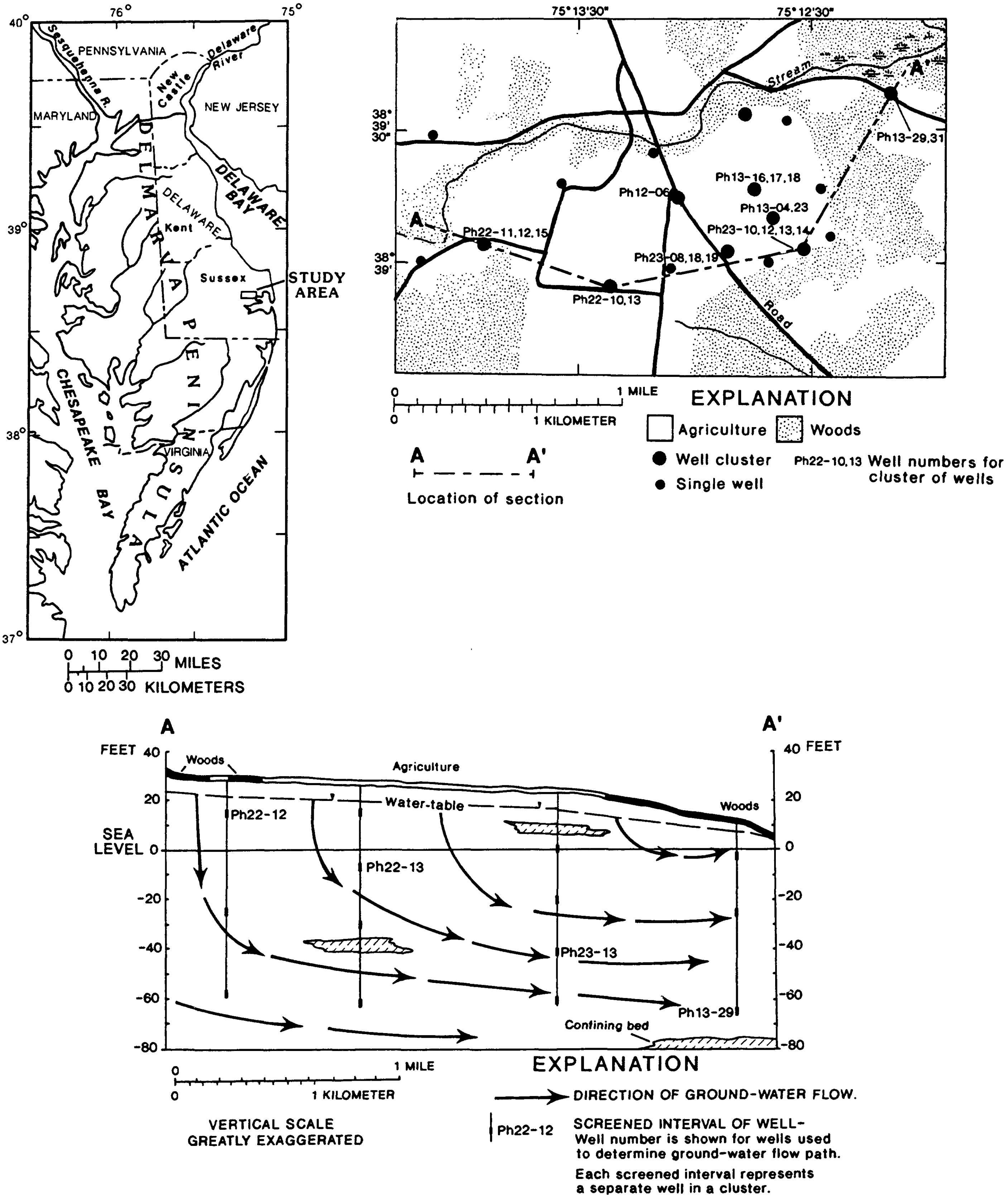
40°
76°
75°
39°
38°
37°
PENNSYLVANIA
NEW JERSEY
MARYLAND
Sesquehanna R.
Delaware River
New Castle
DELMARVA PENINSULA
DELAWARE
Kent
Sussex
DELAWARE BAY
CHESAPEAKE BAY
VIRGINIA
ATLANTIC OCEAN
STUDY AREA
0 10 20 30 MILES
0 10 20 30 KILOMETERS
75°13'30"
75°12'30"
38° 39' 30"
38° 39'
Stream
Road
A
A'
Ph13-29,31
Ph13-16,17,18
Ph12-06
Ph13-04,23
Ph23-10,12,13,14
Ph22-11,12,15
Ph23-08,18,19
Ph22-10,13
0 1 MILE
0 1 KILOMETER
EXPLANATION
Agriculture
Woods
Well cluster
Single well
Ph22-10,13 Well numbers for cluster of wells
Location of section
FEET
40
20
SEA LEVEL 0
-20
-40
-60
-80
Woods
Agriculture
Water-table
Ph22-12
Ph22-13
Ph23-13
Ph13-29
Confining bed
0 1 MILE
0 1 KILOMETER
VERTICAL SCALE GREATLY EXAGGERATED
EXPLANATION
DIRECTION OF GROUND-WATER FLOW.
Ph22-12 SCREENED INTERVAL OF WELL- Well number is shown for wells used to determine ground-water flow path.
Each screened interval represents a separate well in a cluster.

Figure 1. Location of study area; site map showing well locations and hydrogeologic section showing wells along ground-water flow path.

RESULTS AND DISCUSSION

Concentrations of dissolved silica all increased with depth (fig. 2). Denver (1986) attributed the increase to dissolution of silicate minerals, principally feldspars, as water moves through the aquifer. We have used silica concentration as an indicator of relative ground-water age. On the basis of an analysis of ground-water flow, four wells were selected to represent points along a ground-water flow path (fig. 1). These wells are identified in figure 2. The well screen in the well cluster was selected to show the relation pbetween silica concentration and depth, and the increase in ground-water age along the flow path. The age of water from well Ph13-29, from the deepest part of the flow system, was recently estimated from chlorofluorocarbon dating to be at least 25 years (E. Busenberg and L.N. Plummer, U.S. Geological Survey, written commun., 1990). Nitrate concentration in water from well Ph13-29 was 1.5 mg/L (milligrams per liter) as nitrogen. In this area, nitrate concentration has been shown to indicate the extent to which agricultural activity has affected water chemistry (Denver, 1989). Because natural nitrate concentrations are less than 0.4 mg/L as nitrogen, an effect of agricultural activity on ground water in the deeper, older part of the flow system is indicated.

One or more of the three pesticide residues, atrazine, DEA, and DIA were present in all water samples. Concentrations of total atrazine (sum of dissolved atrazine, DEA, and DIA) ranged from trace to 2,830 nanograms per liter (table 1). Concentrations of total atrazine were higher in water from shallow zones (wells screened at a depth of 45 ft and less) and lower in water from deeper zones (table 1). However, highest concentrations of total atrazine were at intermediate depths (wells screened at a depth of 25 to 45 ft).

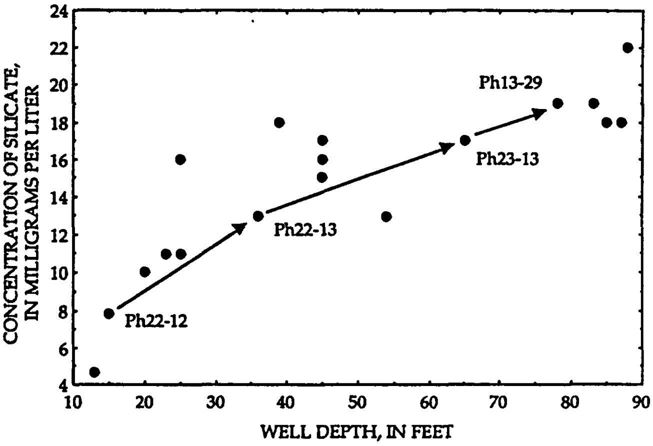

Figure 2. Dissolved silica concentrations as a function of depth. Arrows connect sample wells representing ground-water flow path shown in figure 1.

Nitrate concentrations also were highest at intermediate depths. Variable leaching rates affected by factors such as chemical application rates and timing and amount of recharge may partially explain this trend. High concentrations of nitrate were generally associated with high concentrations of total atrazine (table 1), but nitrate concentration was not always a reliable predictor of total atrazine concentration, possibly because of degradation of atrazine and variability in rates and timing of application of the herbicide compared to that of nitrate.

The DEA concentration was greater than the atrazine concentration in 88 percent of the ground-water samples, and, in some samples, it was the only atrazine component present. This is shown by the increase in ratio of DEA to total atrazine from less than 0.1 in shallow ground water to values between 0.8 and 1.0 in water from deeper zones (fig. 3). DIA was generally a minor component and was not detected in water samples from deeper zones. The predominance of DEA in the ground water is consistent with results of studies of atrazine degradation in soils. These studies have shown that DEA is formed in preference to DIA (Sirons and others, 1973). In addition, in the few studies that include analyses of atrazine metabolites in ground water, DEA was the predominant metabolite identified (Leistra and Boesten, 1989; Pereira and others, 1990).

Changes in the relative amounts of atrazine, DEA, and DIA occur along the ground-water flow path (fig. 4). Atrazine is the major component in water from the shallowest zone (from well Ph22-12); concentrations decrease with depth and position along the flow path. DEA concentration increases in water from intermediate zones along the flow path to well Ph22-13, then decreases steadily. This decrease in atrazine concentration and corresponding increase in DEA concentration may be related to continued degradation of atrazine to DEA as it migrates in ground water. Variations in ground water recharge, and the resulting variable residence time of atrazine in the soil zone, also might contribute to variations in the relative amounts of atrazine and metabolites transported to ground water. In addition to degradation, the decrease in the total concentration of atrazine and its metabolites along the flow path corresponds to a decrease in the effect of agricultural activities with depth in the aquifer because of mixing with water originating in an upgradient forested area (Denver, 1989).

CONCLUSIONS

Changes in the proportions of atrazine and a metabolite, DEA, as water moves through the unconfined aquifer, imply degradation of the parent compound in the ground-water system. Increasing ground-water age along the flow path was demonstrated by analyzing ground-water flow in conjunction with determining the relation between silica concentration and depth. It is noteworthy that the water from the deepest zone in the flow path (from well Ph13-29) contained a trace of DEA, indicating persistence of herbicide residues in the ground-water system for at least 25 years.

The relation between nitrate concentration and total atrazine also implies degradation of the herbicide in the ground-water system. Although high concentrations of nitrate were generally associated with high concentrations of total atrazine in the shallow part of the aquifer, comparably high concentrations of nitrate in the deep part of the aquifer are not associated with high concentrations of total atrazine.

Table 1. *Concentration of atrazine, selected metabolites, and other chemical constituents in water from wells in southeastern Delaware, in December 1989-January 1990*

[ft, feet; mg/L, milligrams per liter; ng/L, nanograms per liter; leaders (--) indicate not detected; Tr, trace means detected but at less than minimum detection limits of 160 ng/L for DIA, 70 ng/L for DEA, and 10 ng/L for atrazine]

Well identification number	Depth (ft)	Dissolved silica (mg/L)	Nitrate as N (mg/L)	DIA (ng/L)	DEA (ng/L)	Atrazine (ng/L)	Total atrazine (ng/L)
Ph12-06	23	11	8	Tr	1,000	890	1,890
Ph13-04	25	16	21	Tr	1,380	1350	2,830
Ph13-16	45	17	24	Tr	840	200	1,040
Ph13-17	60		22	Tr	650	280	930
Ph13-18	85	18	6	--	Tr	Tr	Tr
Ph13-23	45	15	27	Tr	1,190	840	2,030
Ph13-29	78	19	1.5	--	Tr	--	Tr
Ph13-31	39	18	21	Tr	360	Tr	360
Ph22-10	13	4.6	27	323	1,020	440	1,780
Ph22-11	54	13	7.4	--	320	10	330
Ph22-12	15	7.8	20	420	Tr	1780	2,220
Ph22-13	36	13	32	Tr	2,250	160	2,410
Ph22-15	88	22	5.2	--	150	--	150
Ph23-08	20	10	13	220	730	490	1,440
Ph23-10	25	11	38	1,070	310	390	1,770
Ph23-12	45	16	29	Tr	1,170	740	1,910
Ph23-13	65	17	18	--	1,000	210	1,210
Ph23-14	83	19	26	--	470	--	470
Ph23-18	56		21	--	1,240	130	1,370
Ph23-19	87	18	24	--	Tr	Tr	Tr

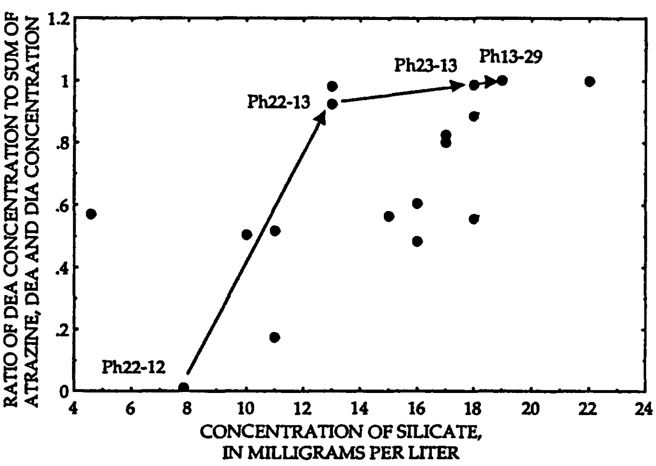

Figure 3. Ratio of DEA concentration to total atrazine (sum atrazine, DEA, DIA) concentration as a function of silica concentration. Arrows identify samples from wells along ground-water flow path shown in figure 1.

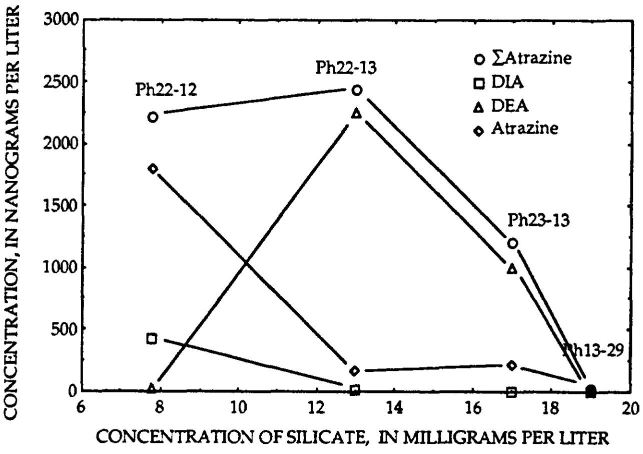

Figure 4. Concentrations of silica, atrazine, DIA, DEA and total atrazine in ground-water samples along flow path.

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RECONNAISSANCE INVESTIGATIONS OF THE EFFECTS OF IRRIGATION DRAINAGE ON WATER QUALITY, BOTTOM SEDIMENT, AND BIOTA IN THE WESTERN UNITED STATES

By Herman R. Feltz[1], Marc A. Sylvester[2], and Richard A. Engberg[3]

ABSTRACT

In response to concerns expressed by the U.S. Congress and others over contamination at the Kesterson National Wildlife Refuge in California, the U.S. Department of the Interior started a program in 1985 to identify the nature and extent of irrigation-induced water-quality problems that might exist in other areas of the Western United States.

An evaluation of the results of completed reconnaissance investigations indicates that selenium is the trace element commonly found at elevated concentrations in water, bottom sediment, and biota, and has the greatest potential to cause toxicological effects in most of the study areas. Impaired bird reproduction and deformed embryos were noticed in 5 of 20 areas studied. Bioaccumulation and biomagnification of selenium is evident in some areas. Elevated concentrations of selenium associated with irrigation drainage can be either localized or widespread.

INTRODUCTION

Irrigation drainwater is known to affect the quality of receiving streams, reservoirs, and wetlands. In most cases, the drainwater merely increases the concentration of dissolved solids and major constituents. In 1983, after deformities, reproductive failure, and mortalities were found among waterfowl and shorebirds at Kesterson National Wildlife Refuge in California, the link was made between irrigation drainage and elevated concentrations of selenium (Presser and Ohlendorf, 1987). Research demonstrated that irrigation water mobilized selenium in soils on the west side of the San Joaquin Valley. Drainwater was carried by tile drains to a canal and impounded in Kesterson Reservoir to augment water supplies for the refuge, which is an artificial wetland with no outlet.

Because of the concern that problems related to selenium or other trace inorganic or organic constituents in irrigation drainage might not be limited to the Kesterson Reservoir area, the U.S. Department of Interior (DOI) began a program in 1985 to determine whether problems related to irrigation existed at other Department constructed or managed irrigation projects, national wildlife refuges, or other wetland areas for which the DOI has responsibilities under the Migratory Bird Treaty Act, the Endangered Species Act, or other legislation. As the program evolved, it has become a five-phase process (Deason, 1986): (1) site identification, (2) reconnaissance investigations, (3) detailed studies, (4) planning, and (5) remediation. Activities in the first three phases are conducted by study teams composed of scientists from the U.S. Geological Survey (USGS), the U.S. Fish and Wildlife Service (FWS), the U.S. Bureau of Reclamation (BOR), and the U.S. Bureau of Indian Affairs. A USGS scientist heads each study team. Activities for phases 4 and 5 are conducted by the BOR.

Site Identification

Historically, approximately 600 irrigation projects and major wildlife resource areas have been constructed or are managed in 17 Western States by DOI Bureaus. Nineteen of these areas were recommended by DOI Bureaus in 1985 for reconnaissance investigations because drainwater from these project areas might contain trace constituents with the potential to cause harmful effects on biota.

Reconnaissance Investigations

Reconnaissance investigations are studies designed to determine whether (1) irrigation drainage has caused or has the potential to cause significant harmful effects on human health or on fish and wildlife, or (2) may reduce the suitability of water for beneficial uses. The duration of reconnaissance investigations is approximately 2 years.

To enhance comparability of results among the study areas, the investigations are guided by a common protocol for obtaining data. However, study designs differ because of hydrologic and geochemical conditions and unique ecological systems in each area. Sampling sites are determined by the individual study teams. Samples of water, bottom sediment, and biota generally are collected before, during, and after the irrigation season. Samples of each medium are analyzed for major constituents and trace elements including arsenic, barium, boron, cadmium, chromium, copper, lead, mercury, molybdenum, nickel, selenium, silver, uranium, vanadium, and zinc. Pesticide analyses are performed at the discretion of study teams.

Detailed Studies

Detailed studies are initiated if reconnaissance investigations indicate that potentially serious water-quality problems are related to irrigation drainage. The purpose of detailed studies is to gather sufficient information to provide the scientific understanding needed for development of reasonable alternatives to mitigate or resolve identified problems.

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[1] U.S. Geological Survey, Reston, Va.

[2] U.S. Geological Survey, Menlo Park, Calif.

[3] U.S. Department of the Interior, Washington, D.C.

Whereas reconnaissance investigations are designed to study the location and amounts of potentially toxic constituents, detailed studies are tailored specifically to each individual area, and include the identification of sources, transport mechanisms, and fate of potentially toxic constituents, as well as food-chain studies and quantification of adverse effects.

Planning

The purpose of planning is to develop coordinated action for cleanup with appropriate Federal, State, and local agencies. When a reconnaissance investigation indicates that potentially serious problems exist and that detailed study is needed, it generally implies that the final two phases of the program will be required at the site.

Remediation

The final phase involves implementation of corrective actions developed during the planning process. Although not specifically a part of this program, Kesterson Reservoir currently is in the remediation stage.

SUMMARY OF RESULTS

Reconnaissance Investigations

Since the DOI Irrigation Drainage Program began, a total of 24 reconnaissance investigations have been or currently are being conducted (fig. 1). Nine reconnaissance investigations started in 1986 are complete and reports have been published.

Reconnaissance investigations for 11 additional areas were started in 1988. Field work, laboratory analysis, and data interpretation are complete. Some reports are published and the remainder are in various stages of preparation.

An analysis of information from reconnaissance indicated that significant irrigation drainage-related water-quality problems existed in several areas (Sylvester and others, 1988; Feltz and others, 1990). Continuing study in the Tulare Lake Bed area was incorporated into an existing program in the San Joaquin Valley of California. Four other areas warranted detailed study in the DOI Program: Salton Sea, Calif.; Stillwater Wildlife Management Area, Nev.; Middle Green River basin, Utah; and Kendrick Reclamation Project, Wyo.

Detailed Studies

Detailed studies of 3-years duration began in 1988 in each area. Elevated concentrations of selenium in water, bottom sediment, and biota were the principal concern except in the Stillwater Wildlife Management Area (WMA) where elevated arsenic concentrations were the major concern. Field work for these studies was completed in 1990 and reports are in review.

Comparison of Selenium Concentrations Among Study Areas

Selenium, the constituent most commonly found at elevated concentrations, has the greatest potential for toxicological effects in most of the study areas. Selenium data are compared to (1) U.S. Environmental Protection Agency maximum contamination levels (MCL) in drinking water and water-quality criteria for protection of aquatic life, (2) baselines for soil and fish, (3) a threshold concentration for adverse reproductive effects in fish, and (4) concentrations in bird livers and eggs associated with toxicity based on laboratory dietary studies and field investigations published in scientific literature.

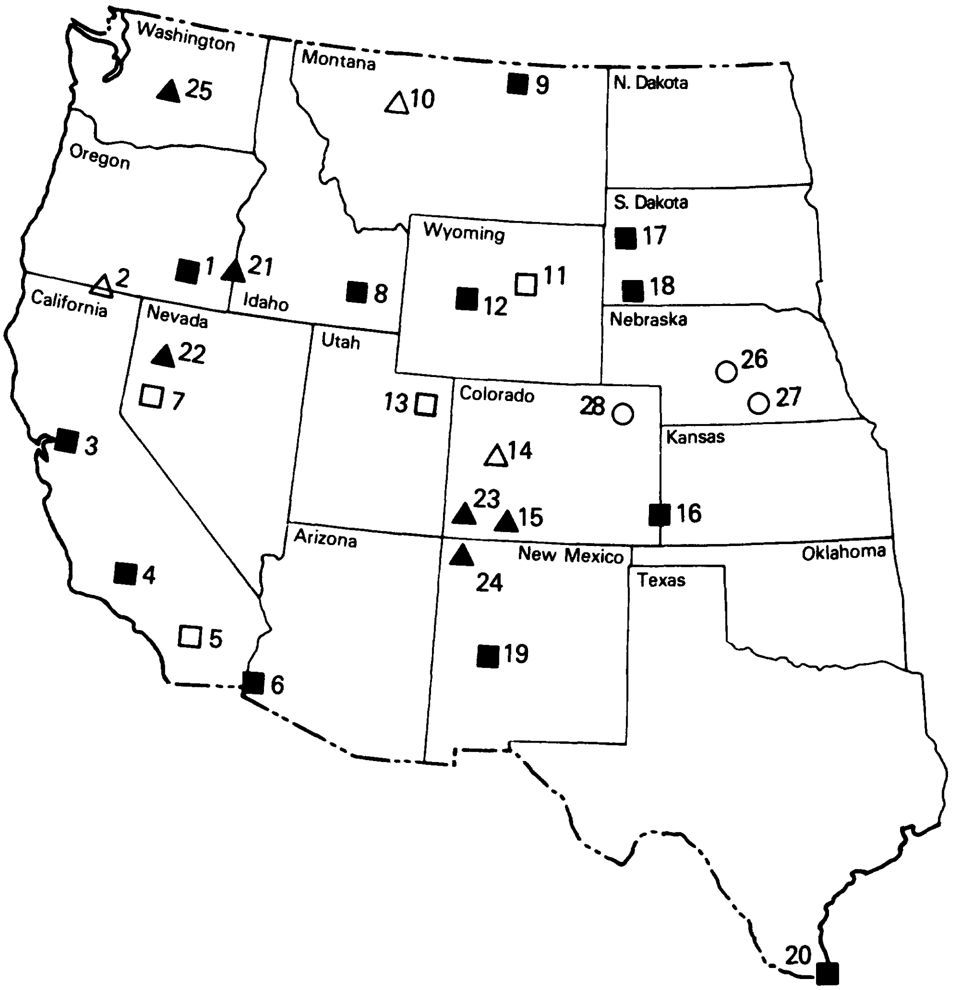
The following discussion is based on all analytical results for selenium in each area. Thus, results for reference, irrigation supply, drainwater, and receiving water (streams, ponds, wetlands, and playas) are included. For fish and birds, results for species were combined for each area to allow a comparison among areas. Because the same species could not be collected in all study areas, sufficient data were not available to compare data distributions for each species among study areas. Comparisons of fish and bird data among study areas are made with the understanding that there are species-to-species differences in selenium uptake and effects that might limit the validity of comparisons.

Selenium in Water

Selenium concentrations in water (fig. 2A) generally were less than the U.S. Environmental Protection Agency (1986) MCL for drinking water (10 µg/L (micrograms per liter)) and the U.S. Environmental Protection Agency (1987) freshwater acute criterion for protection of aquatic life (20 µg/L). Water samples from the Tulare Lake Bed area and Middle Green River basin had median selenium concentrations that exceeded 20 µg/L. Samples from the Salton Sea area, Kendrick Reclamation Project area, and the Gunnison River basin had 75th-percentile concentrations that exceeded 20 µg/L. The maximum selenium concentration observed was 4,400 µg/L in an abandoned well in the Pine River area. The next largest selenium concentration was 580 µg/L in a seep drain ditch in the Sun River area.

Selenium in Bottom Sediment

With three exceptions, concentrations of selenium in bottom sediment (fig. 2B) were less than the upper limit of the expected 95-percent baseline range (1.4 µg/g (micrograms per gram)), dry weight) for selenium in soils of the Western United States (R.C. Severson, U.S. Geological Survey, written commun., 1987, based on information in Shacklette and Boerngen, 1984). The Kendrick Reclamation Project area, Middle Green River basin, and Gunnison River basin had extremely large concentrations of selenium in bottom sediment (25-85 µg/g).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EXPLANATION

■ RECONNAISSANCE INVESTIGATIONS COMPLETED

1. Malheur National Wildlife Refuge, Oreg.
3. Sacramento Refuge Complex, Calif.
4. Tulare Lake Bed Area, Calif.
6. Lower Colorado River Valley, Calif./Ariz.
8. American Falls Reservoir, Idaho
9. Milk River Basin, Mont.
12. Riverton Reclamation Project, Wyo.
15. Pine River Area, Colo.
16. Middle Arkansas River Basin, Colo./Kans.
17. Belle Fourche Reclamation Project, S. Dak.
18. Angostura Reclamation Unit, S. Dak.
19. Middle Rio Grande and Bosque del Apache National Wildlife Refuge, N. Mex.
20. Lower Rio Grande Valley and Laguna Atascosa National Wildlife Refuge, Tex.

□ RECONNAISSANCE AND DETAILED STUDIES COMPLETED

5. Salton Sea Area, Calif.
7. Stillwater Wildlife Mgmt. Area, Nev.
11. Kendrick Reclamation Project Area, Wyo.
13. Middle Green River Basin, Utah

▲ RECONNAISSANCE INVESTIGATIONS UNDERWAY

21. Owyhee-Vale Projects, Oreg./Idaho
22. Humboldt Wildlife Mgmt. Area, Nev.
23. Dolores Project, Colo.
24. San Juan River Area, N. Mex.
25. Upper Columbia Basin, Wash.

△ RECONNAISSANCE COMPLETED AND DETAILED STUDIES UNDERWAY

2. Klamath Basin Refuge Complex, Calif./Oreg.
10. Sun River Area, Mont.
14. Gunnison River Basin/Grand Valley Project, Colo.

○ POTENTIAL RECONNAISSANCE INVESTIGATIONS

26. Central Nebraska Project, Nebr.
27. Bostwick Division, Nebr./Kans.
28. Colorado-Big Thompson, Colo.

Figure 1. Locations and names of study areas.

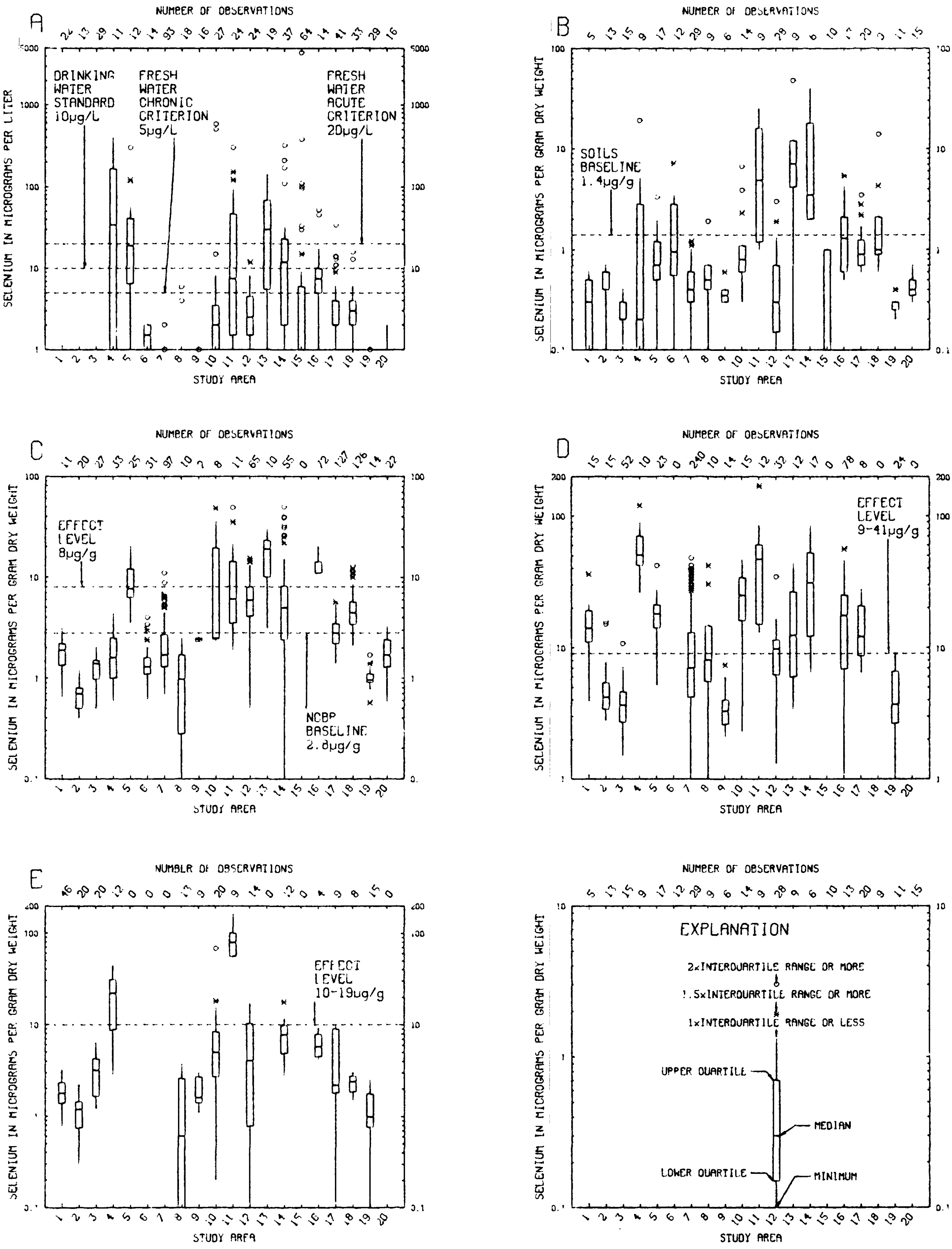

Figure 2. Comparison of selenium concentrations in: A. water; B. bottom material; C. fish; D. bird livers; E. bird eggs. NCBP (National Contaminant Biomonitoring Program).

Selenium in Fish

Selenium concentrations in fish (fig. 2C) in most areas exceeded the 85th-percentile baseline of 2.8 µg/g, dry weight, established by the National Contaminant Biomonitoring Program of the FWS (Lowe and others, 1985, p. 370). Selenium concentrations in 9 of 20 areas exceeded the threshold concentration (about 8.0 µg/g, dry weight) for adverse reproductive effects in fish (Baumann and May, 1984, p. 7-7). Seleniferous cretaceous marine shales are prevalent in all areas except the Salton Sea area and the Stillwater WMA. Volcanic rocks probably are a source of selenium in the Stillwater WMA. Bioaccummulation of selenium is indicated by increased concentrations from water to fish in all areas, and from bottom sediment to fish in six of the nine areas having selenium concentrations in fish that might cause adverse reproductive effects.

Selenium in Bird Livers

Most concentrations of selenium in bird livers (fig. 2D) were within the levels (9-41 µg/g, dry weight) associated with adverse reproductive effects in mallards (reduced egg laying and chickling survival) based on laboratory dietary studies (Heinz and others, 1987, p. 7). Concentrations greater than 30 µg/g are likely to cause embryo deformities in birds (Skorupa and others, 1990). Selenium concentrations in bird livers exceeded 30 µg/g, dry weight, in the Malheur National Wildlife Refuge, Tulare Lake Bed area, Salton Sea area, Stillwater WMA, American Falls Reservoir area, Sun River area, Kendrick Reclamation Project area, Riverton Reclamation Project area, Middle Green River basin, Gunnison River basin, and Middle Arkansas River basin. Reproductive impairment and deformities in birds have been observed in the Tulare Lake Bed area, Stillwater WMA, Sun River area, Kendrick Reclamation Project area, and Middle Green River basin.

Selenium in Bird Eggs

Selenium concentrations in bird eggs (fig. 2E) generally were less than concentrations (10-19 µg/g, dry weight) associated with deformities and reduced survival in mallards based on laboratory dietary studies (Heinz and others, 1987, p. 7). However, concentrations exceeded 10 µg/g, dry weight, in the Tulare Lake Bed area, Sun River area, Kendrick Reclamation Project area, Riverton Reclamation Project area, and the Gunnison River basin. Deformed birds were observed in the Tulare Lake Bed area, Kendrick Reclamation Project area, and Sun River area. Biomagnification in the food chain was indicated in the Sacramento Refuge Complex, Tulare Lake Bed area, Sun River area, and Kendrick Reclamation Project area because selenium concentrations in bird eggs were greater than selenium concentrations in fish.

GENERAL OBSERVATIONS AND RELATIONS

As reported by Sylvester and others (1988) and Feltz and others (1990), results of the reconnaissance investigations have shown that irrigation-drainage problems are prevalent in the Western United States. Elevated concentrations of trace elements have been detected in most study areas, and elevated concentrations of pesticides have been detected in some study areas. Selenium is the trace element most commonly found at elevated concentrations in water, bottom sediment, and biota. However, boron, arsenic, uranium, and mercury also were found at elevated concentrations. DDE, a metabolite of DDT, was the only pesticide residue commonly found at elevated concentrations.

In the work reported here, concentrations of selenium in fish and birds were large enough in several study areas to have the potential to cause toxicological effects even when selenium concentrations in water and bottom sediment were low. Impaired bird reproduction and embryo deformities have been noted in 5 of the 20 study areas. Bioaccumulation and biomagnification of selenium is evident in some areas. Elevated concentrations of constituents associated with irrigation drainage can be localized (for example, Sun River area), but in another area, elevated concentrations may be widespread (for example, Stillwater WMA).

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SOURCES, SINKS, AND EFFECTS OF SELENIUM AT STEWART LAKE WATERFOWL MANAGEMENT AREA, JENSEN, UTAH

By Doyle W. Stephens[1], Bruce Waddell[2], and Jerry B. Miller[3]

ABSTRACT

Soils in the area of Stewart Lake are derived from alluvium and Mancos Shale and contain concentrations of total selenium ranging from 200 to 3,000 parts per billion. Subsurface drains constitute the only source of surface inflow to Stewart Lake. During 1986-89, the median concentration of selenium in water discharging from the drains was 43 micrograms per liter and was associated with drainage from soils developed on Billings clay. Stewart Lake acts as a sink for selenium discharged by the drains. Median concentrations of selenium discharged by every drain exceeded the standard of 5 micrograms per liter established by the State for the protection of aquatic wildlife, but the standard was exceeded in only 64 percent of the samples from the outflow of the lake. Only 25 percent of the daily load of 252 grams of selenium entering the lake was discharged to the Green River. Nineteen percent of randomly collected duck eggs collected from Stewart Lake contained concentrations of selenium that exceeded 15 micrograms per gram, a concentration associated with deformities in mallard embryos. Several deformed duck embryos were found within the area and concentrations of selenium in livers of a coot and a mallard from Stewart Lake exceeded 19 micrograms per gram, a concentration associated with deformities at Kesterson National Wildlife Refuge in California.

INTRODUCTION

This paper presents the results of a study done from 1986 through 1989 of the sources and sinks of selenium, and its effects on the biota at a State waterfowl refuge near Jensen, Utah. The study was part of a larger investigation of irrigation-related contamination of waterfowl areas near the Green River that was done as part of the Irrigation Drainage Program of the U.S. Department of Interior (Stephens and others, 1988, 1989). Stewart Lake Waterfowl Management Area (WMA) is located adjacent to the Green River, 19 km (kilometers) southeast of Vernal near Jensen, Utah (fig. 1). The lake has a surface area of 100 ha (hectares) and is managed by the Utah Division of Wildlife Resources.

Geology, Irrigation, and Drainage

Mancos Shale containing gypsum, epsomite, and other minerals is the dominant formation in the Jensen area and is greater than 1,500 m (meters) thick (Untermann and Untermann, 1954, p. 63). Soils in the area are derived from weathering of Mancos Shale and from alluvial material transported into the area by the Green River. Laronne (1977, p. 70) reported terraces of Mancos Shale often contained 0.3 to 1.7 percent soluble salts, predominantly gypsum. Large concentrations of selenium may be asociated with the gypsum. Samples of Mancos Shale from western Colorado contained total selenium concentrations of 2,000 to 6,000 ppb (parts per billion) (Williams and Byers, 1935, p. 432).

Red Fleet Reservoir, 27 km north of Jensen, provides irrigation water for about 1,600 ha near Stewart Lake. Five subsurface drain lines were installed on 300 ha in Jensen by the U.S. Bureau of Reclamation during 1974-79 to remove excess irrigation water from poorly drained soils and to provide water to Stewart Lake as mitigation for the upstream diversion of water from Ashley Creek. Since 1979, the only source of surface inflow to Stewart Lake has been discharge from the drains. The outflow from Stewart Lake enters the Green River.

SOURCES OF SELENIUM

Association With Specific Soil Types

Strahorn and others (1924) mapped 19 soil types during a soil survey of the Jensen area and adjacent Ashley Creek. Two of the soils, the Billings series, derived from Mancos Shale, and the Naples series, which locally is underlain by soils of the Billings series, comprise most of the soils near Jensen. Large concentrations of selenium in water samples collected from springs, shallow wells, and subsurface drains in the Jensen area and near Ashley Creek are associated primarily with soils developed on Billings clay and secondarily with the Naples loam.

Selenate reacts like sulfate in soils and is not as strongly adsorbed as selenite is by soil minerals, such as goethite (Neal and Sposito, 1989, p. 73). However, the amount of the selenate that may be extracted by water is quite variable. Saturation extracts of two samples of Mancos Shale from the Jensen area yielded 4 to 31 percent of the total selenium content. Irrigated soils in the Jensen area contained concentrations of selenium ranging from 200 to 3,000 ppb (table 1). Typically, less than 5 percent of the total selenium in the Jensen soils was extractable by water. Other studies have shown that water-soluble selenium represents about 2 to 10 percent of the total selenium present in soils (Berrow and Ure, 1989, p. 230).

Ground Water

Movement of shallow ground water in the Jensen area is generally to the south and east toward Stewart Lake WMA and the Green River. Local ground-water flow in the area is bounded vertically by the relatively impermeable Mancos Shale, and little if any water rises through the shale (Hood, 1977, p. 8). Concentrations of selenium in shallow wells in the Jensen area ranged from <1 to 360 µg/L

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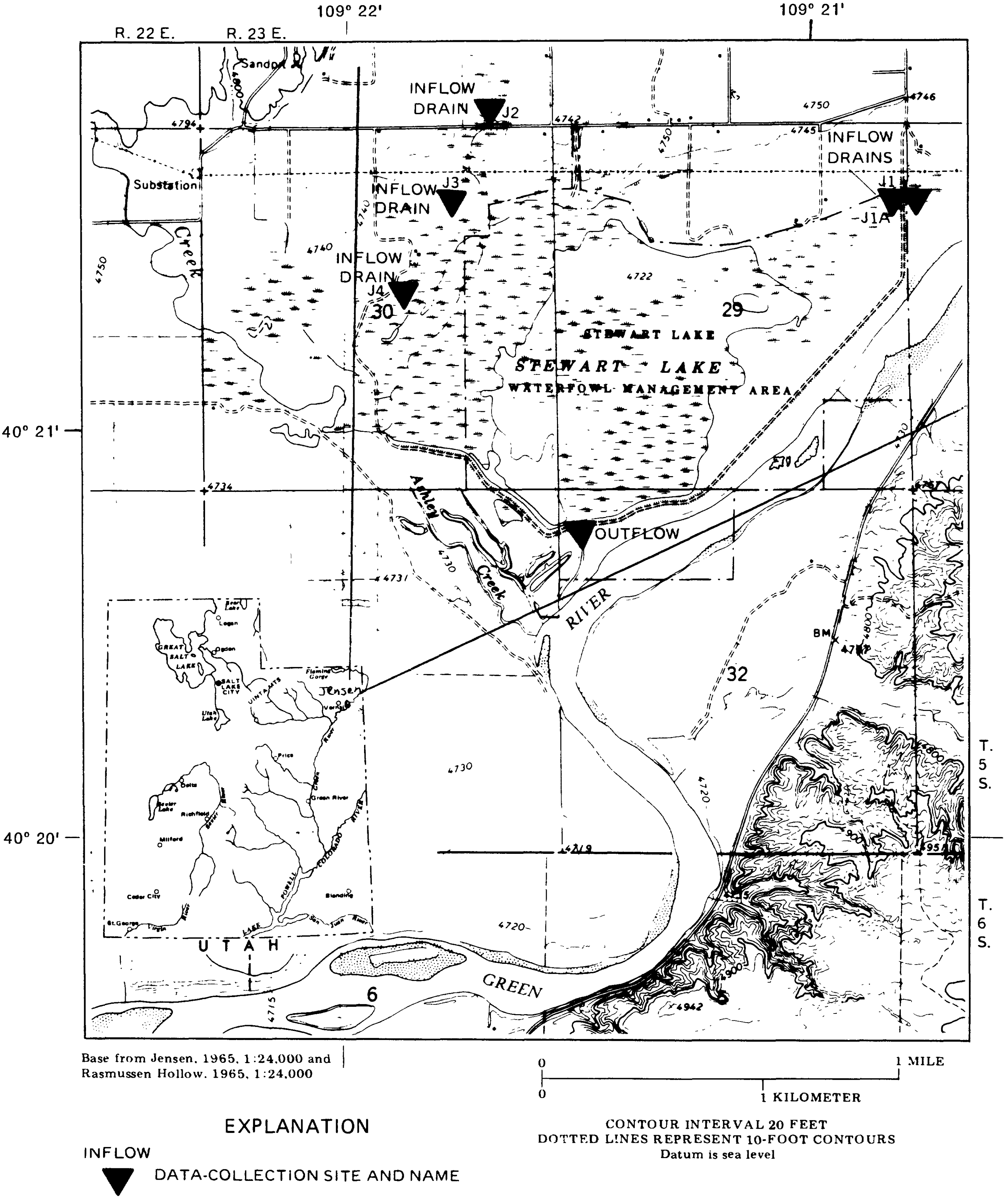
[1] U.S. Geological Survey, Salt Lake City, Utah
[2] U.S. Fish and Wildlife Service, Salt Lake City, Utah
[3] U.S. Bureau of Reclamation, Salt Lake City, Utah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INFLOW DRAINS J1 J1A
OUTFLOW
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STEWART LAKE WATERFOWL MANAGEMENT AREA
Substation
Sandon
Creek
Ashley Creek
GREEN RIVER
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Vernal
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Price
Green River
Delta
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EXPLANATION
INFLOW
▼ DATA-COLLECTION SITE AND NAME

Figure 1. Data-collection sites at Stewart Lake Waterfowl Management Area.

Table 1. *Sources and concentrations of selenium near Stewart Lake Waterfowl Management Area*
[<, less than]

Source	Selenium concentration, parts per billion: Median	Selenium concentration, parts per billion: Range	Number of samples
Irrigated soils	950	200-3,000	44
Mancos shale	2,550	1,100-4,000	2
Soil efflorescence	2,300	-	1
Shallow ground water			
All wells	14.5	< 1- 360	46
J1 drain area	<1	< 1- 15	13
J1a drain area	12.5	< 1- 19	6
J2 drain area	48	10- 360	8
J3 drain area	110	80- 140	5
J4 drain area	20	2- 60	14
Drainwater	43	4- 140	62

(micrograms per liter) and the larger concentrations generally were present in wells located within drain areas for the J2, J3 and J4 drains (table 1). These drains also discharged the largest concentrations of selenium to Stewart Lake (fig. 2). Hydraulic conductivities through the soils were highly variable but the typical velocity of water moving through the soils ranged from about 4.5 to 7.3 centimeters per day. Water applied to the land surface could take from 3.5 to 5.6 years to reach a drain lateral.

SINKS FOR SELENIUM

Selenium in the Inflow and Outflow of Stewart Lake

Stewart Lake acts as a sink for selenium discharged by the drains. Median concentrations of selenium from every drain exceeded the 5 µg/L standard established by the State of Utah for the protection of aquatic wildlife (fig. 2). However, the lake retained a sufficient quantity such that the selenium concentration in water discharging to the Green River exceeded the standard of 5 µg/L in only 80 percent of the samples. The largest concentrations, and generally the largest variability, were found in water from drains J3 and J4.

The total amount of selenium retained by Stewart Lake is substantial. Table 2 shows a comparison of the median concentrations and loads of chloride, a conservative constituent, compared to medians for selenium, a nonconservative element. Stewart Lake discharges a total daily load of chloride of 276 kg/d (kilograms per day)--about equal to the total daily load of 255 kg/d entering the lake through the drains. However, only 25 percent of the total load of 252 g (grams) of selenium entering the lake discharged to the Green River. Almost 200 g of selenium per day were retained by the lake as sedimentary deposits and incorporated into microbes and plants. For example, concentrations of

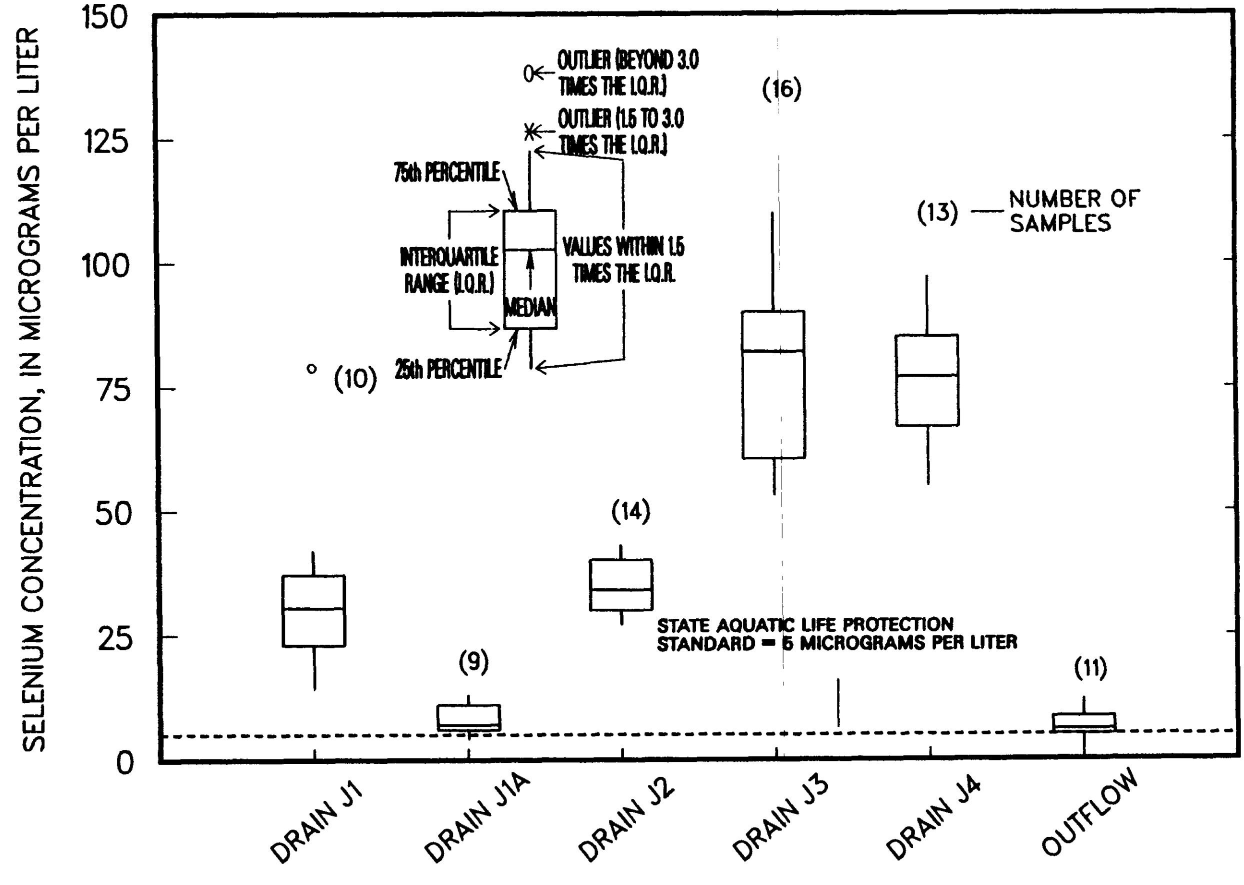

Figure 2. Concentrations of selenium in water from agricultural drains discharging to Stewart Lake and in the outflow from the lake, water years 1986 through 1989.

Table 2. *Comparison of median discharges, median concentrations of chloride and selenium, and loads of chloride and selenium in drainwater entering Stewart Lake and in the outflow from the lake*

[Discharge for the outflow and concentration data for all sites are for water years 1988-89. Discharge for all drains for period of record. (The selection of a recent period for the outflow was done to avoid the years from 1983-87 when the Green River flooded Stewart Lake.) L/s, liters per second; mg/L, milligrams per liter; µg/L, micrograms per liter; kg, kilograms; g, grams; kg/d, kilograms per day; g/d, grams per day.]

Site	Discharge (L/s)	Chloride		Selenium	
		Concentration (mg/L)	Load (kg/d)	Concentration (µg/L)	Load (g/d)
Drains J1,J1a	[1]28.0	[2]35	84.79	[2]30.5	73.89
Drain J2	22.0	28	53.44	34	64.89
Drain J3	11.3	68.5	67.06	77	75.38
Drain J4	5.9	96.5	49.61	74	38.04
Total inflow load			254.9		252.2
Outflow	138.8	23	275.8	5	60

[1] Discharge is combined for J1 and J1a drain.

[2] Concentration is for the J1 drain.

selenium in bottom sediment near the J3 drain outfall declined from 140 µg/g (micrograms per gram), 20 m from the outfall, to 11 µg/g, 800 m from the outfall. Concentrations in cattail root followed the same pattern.

EFFECTS OF SELENIUM ON BIOTA

Mortality of juveniles and adults and adverse effects on reproduction, such as deformed larval stages and embryos, are the principal toxic effects observed in fish and birds when large concentrations of selenium are present in aquatic environments (Lemly and Smith, 1987). In water-birds, deformities typically involve missing eyes; curled or shortened lower beaks, truncated legs, commonly with no feet or nails, and formation of the brain external to the cranium. These types of deformities were associated with selenium concentrations of 19 to 130 µg/g (dry weight) in livers of birds from Kesterson National Wildlife Refuge (NWR) in California (Ohlendorf and others, 1986, p. 49). Under laboratory conditions, teratogenesis or death of embryos was observed in mallards when concentrations of selenium in the eggs reached 15 to 20 µg/g (dryweight) (Heinz and others, 1987).

Death and deformities represent only the most overt signs of selenium toxicity. Concern for reduced reproductive success in waterfowl have been reported to occur when concentrations of selenium in water are as small as 2 to 5 µg/L (Lemly and Smith, 1987, table 2).

Waterfowl

Only 49 percent of the 35 nests where the fate of the eggs was known were believed to be successful (at least 1 egg hatched). Deformed embryos were observed in possibly two nests. Deformities were clearly observed in a redhead embryo with a whole-body concentration of selenium of 3.9 µg/g. The second nest was that of a teal and confirmation of deformities was limited by the decomposition of the embryo.

Selenium concentrations in 49 eggs collected at Stewart Lake WMA ranged from 2 µg/g for a Canada goose to 33 µg/g for a western grebe. Summary concentrations of selenium in randomly collected eggs from four species of duck (cinnamon teal, gadwall, mallard, and redhead) from Stewart Lake WMA were compared to summary concentrations for the same four species from Leota Bottom, an uncontaminated area at Ouray NWR, 48 km south of Stewart Lake (fig. 3). Nineteen percent of the eggs from Stewart Lake WMA contained selenium concentrations that exceeded 15 µg/g, a value associated with deformities in mallard embryos. Concentrations of selenium in eggs from Leota Bottom were significantly smaller and were less than concentrations associated with teratogenic effects on embryos. Concentrations of selenium in the livers of American coots and mallards collected from Stewart Lake WMA were compared to concentrations of selenium in the same species collected during the same seasons at Leota Bottom (fig. 3). Concentrations of selenium in livers of a coot and mallard from Stewart Lake WMA exceeded 19 µg/g, the smallest value associated with deformities at Kesterson NWR.

Fish

Selenium can cause substantial mortality of fish eggs, deformities in larvae, and direct mortality of juveniles and adults (Eisler, 1985). At sublethal concentrations, adverse effects may slowly remove upper- trophic-level fish (predators) from the system. In a synopsis of existing studies, (Lemly and Smith, 1987, table 2), reported reproductive failures in several fish species were associated with whole-body residues of selenium that equaled or exceeded 12 µg/g dry weight.

The fishery in Stewart Lake consisted primarily of carp and black bullheads. Predatory fish such as bluegill and green sunfish were rare. The median concentration of selenium in all carp was 33.5 µg/g, considerably larger than reference values for concentrations known to have adverse effects on some fish species.

When concentration data for selenium in all species of fish from Stewart Lake were combined, fish collected near the drains (northshore) contained a significantly larger concentration of selenium than fish collected near the outlet (southern shore). The species composition sampled at each site was approximately the same. The large concentrations of selenium in fish and waterfowl from Stewart Lake prompted the Utah Department of Health to issue a health advisory in 1988, recommending that adult males consume no more than 283 g of fish or waterfowl from Stewart Lake WMA per week.

SUMMARY

Soils in the area of Stewart Lake are derived from alluvium and the Mancos Shale. Soils associated with the shale drain poorly and contain concentrations of total selenium ranging from 200 to 3,000 ppb. Five subsurface drains were installed by 1979 to improve drainage in irrigated soils. Drainwater constitutes the only source of

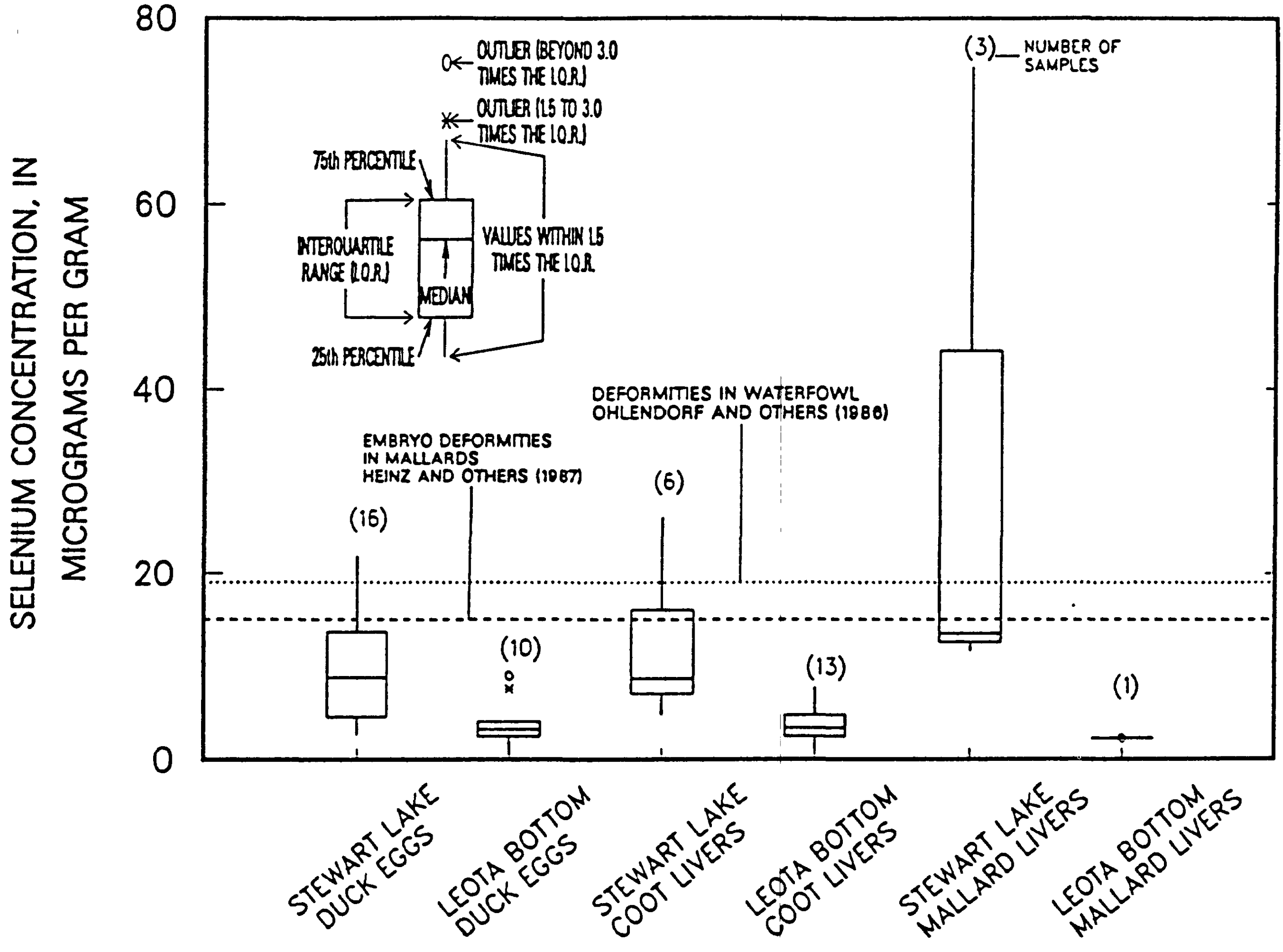

Figure 3. Concentrations of selenium in randomly-collected waterfowl eggs and liver samples of American coots and mallards collected from Stewart Lake Waterfowl Management Area and from Leota Bottom at Ouray National Wildlife Refuge.

surface inflow to Stewart Lake. The median concentration of selenium in ground water from shallow wells in the Jensen area was 14.5 µg/L. The median concentration of selenium in drainwater discharging to Stewart Lake was 43 µg/L.

Stewart Lake acts as a sink for selenium discharged by the drains. Although median concentrations of selenium discharged by every drain exceeded the 5-µg/L standard established by the State for the protection of aquatic wildlife, concentrations in only 80 percent of the samples from the outflow of the lake exceeded the standard. Only 25 percent of the daily load of 252 g of selenium entering the lake discharged to the Green River.

Nineteen percent of randomly collected duck eggs collected from Stewart Lake contained concentrations of selenium that exceeded 15 µg/g-- a concentration associated with deformities in mallard embryos. Concentrations of selenium in livers of a coot and a mallard from Stewart Lake WMA exceeded 19 µg/g, the smallest value associated with deformities at Kesterson NWR.

Fish collected near the drains contained significantly larger concentrations of selenium than fish collected on the opposite side of the lake near the outflow. The large concentrations of selenium in fish and waterfowl from Stewart Lake prompted the Utah Department of Health to issue a health advisory in 1988, recommending adult males consume no more than 283 g of fish or waterfowl per week.

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METHOD FOR THE SYSTEMATIC EVALUATION OF ORGANIC CHEMICAL RETENTION BY SOLID-PHASE-EXTRACTION COLUMNS

By Paul D. Capel[1] *and* Daniel S. Barbeau[2]

ABSTRACT

A simple method for evaluating the breakthrough of organic chemicals from solid-phase-extraction columns is suggested. This method is applicable to a wide range of solid-phase-extraction columns, organic chemicals, solution characteristics, and flow rates. The method employs a six-port injection valve and an air-tight solid-phase-extraction column holder placed between a high performance liquid chromatography pump and detector. A typical frontal chromatography (breakthrough) experiment is conducted. The aqueous mobile phase has the appropriate analyte and solution characteristics (pH, ionic strength, solvent modifier, analyte concentration). Breakthrough of the analyte from the solid-phase-extraction column is monitored in real time by the detector trace. The usefulness and limitations of this method are illustrated with deisopropyl atrazine, a polar metabolite of atrazine, which is moderately retained by a octadecyl-modified silica gel. The effects of ionic strength, pH, analyte concentration, organic modifier concentration, flow rate, and column size are evaluated.

INTRODUCTION

Solid-phase extraction (SPE) has been shown to be extremely useful in the isolation, concentration, and fractionation of organic chemicals from solution. The disposable, silica-based, bonded-phase extraction columns are becoming increasingly important (Junk, 1987). These bonded phases are available in a wide variety of organic functional groups that use various molecular interactions (hydrophobic, ion exchange, acid/base, silanol, and so forth). By far the most common interaction reported in the literature is hydrophobic bonding of organic molecules to alkyl or aromatic bonded phases.

SPE is virtually frontal chromatography. The mobile phase, which is usually an aqueous solution of the analyte(s) to be isolated, concentrated, and (or) fractionated, is continuously fed to the column at a constant flow rate. The increasing volume of mobile phase passed through the SPE column moves the active zone of sorption toward the effluent end of the column (Weber, 1972). Initially, the analyte is completely removed from the mobile phase. At some volume, the analyte breaks through and begins to escape from the column. This volume is based on the capacity factor, ké, which is defined as

$$k' = \frac{\text{number of moles of analyte on the stationary phase } (N_s)}{\text{number of moles of analyte in the mobile phase}}$$

The effluent concentration gradually increases with increasing volume until, finally, the influent and effluent concentrations are equal. An "S-shaped" curve typically is observed when the effluent concentration is plotted against volume. For use with environmental water samples, the volume of mobile phase passed through the SPE column is generally smaller than the breakthrough volume. For analytes which have low capacity factors (k' less than 10), SPE is not useful.

A number of possible factors can affect the capacity factor and, therefore, the efficiency of a SPE column for a given analyte. The solution parameters include hydrogen ion (that is, pH) (Shoup and Mayer, 1982; DiCorcia and others, 1989), salt (Andrews and Good, 1982; Hinckley and Bidleman, 1989), dissolved organic carbon (Landrum and others, 1984; Oehmichen and others, 1987), organic modifier (Puyear and others, 1981; Andrews and Good, 1982), and analyte concentration. Other factors are flow rate (DiCorcia and others, 1989) and the type and mass of the bonded phase. Although each of these factors have been considered individually in the literature, no systematic approach has been undertaken to examine their quantitative effects. This paper suggests a simple method for the independent evaluation of each factor affecting the efficiency of an SPE column. The method can be used to evaluate the effects of flow rate, pH, ionic strength, modifier concentration, analyte concentration, and column size on the extraction efficiency of deisopropyl atrazine (DIA) (2-chloro, 4-amino, 6-ethyl-amino-sym-triazine), a common metabolite of the herbicide atrazine, on an octadecyl-modified silica gel.

METHODS

Chemicals and Solutions

Three sizes (100, 500, and 5,000 mg (milligrams)) of octadecyl SPE columns were used in this study (Analytichem International[3]). A stock solution of DIA was made in methanol at a concentration of 299 micrograms per milliliter. Solutions for each test run were made by adding the appropriate amount, usually a few microliters, of the DIA stock solution to degassed water. The addition of the stock solution did not add a significant amount of methanol to the aqueous solutions. The various test solutions contained different amounts of DIA, methanol, sodium chloride (NaCl), and phosphate buffers, to test for the effects of analyte, solvent modifier, salt, and hydrogen ion concentrations.

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Equipment

Equipment for this study consisted of five parts. An HPLC pump (Waters model M-6000) was used to control the flow rate of the aqueous test solution. The signal from a variable wavelength detector (Waters model 450) set at 220 nanometers was sent to an electronic integrator (Hewlett-Packard model 3393a). A six-port valve (Rheodyne model 7010) was in-line between the pump and detector. At the top of the SPE column, the holder consisted of two stainless-steel plates. The upper plate had a 1/16-inch female fitting on top and a groove for a rubber washer on the bottom. The lower plate had one center hole through which the SPE column fit. The plates clamped around the top of the SPE column with three screws making an air-tight seal. The luer end of the SPE column was attached to a Kel-F luer adapter.

Procedure

The octadecyl SPE columns were placed on a vacuum elution system and washed with 2 mL (milliliters) diethyl ether, followed by 2 mL methanol and 6 mL water. For each test run, the cleaned SPE column was filled with the aqueous test solution by a disposable pipette and attached to the column holder. Initially, the six-port valve was positioned so that the flow bypassed the SPE column and went directly to the detector. The integrator was started and a baseline established at 80 percent full scale. After a few minutes of a stable baseline, the six-port valve was turned to direct the flow through the SPE column. The baseline fell in response to the removal of the analyte by the SPE column. The breakthrough of the analyte was followed by the rise in the integrator's baseline until it approached the original baseline (80 percent full scale). Finally, the original baseline was reestablished by turning the six-port valve and diverting the flow from the column to the detector. Breakthrough volumes were calculated at effluent concentrations of 10, 50, and 90 percent of the influent concentration. Capacity factors were calculated based on the number of moles of DIA on the stationary phase (N_s) at 100-percent breakthrough. Assuming that the breakthrough curves are a perfect "S-shape," the number of moles of DIA at 100-percent breakthrough was calculated by multiplying the volume of water that passed through the SPE column at 50 percent breakthrough times the influent concentration. Although many of the curves were very close to this ideal, some of them exhibited some chromatographic tailing, which would yield an underestimation of N_s and k'.

RESULTS AND DISCUSSION

Effect of Solution Parameters on Breakthrough Volume

Breakthrough volumes and capacity factors (k') of DIA as a function of ionic strength were measured in aqueous solutions representing the complete range from freshwater (0 grams NaCl per liter) to seawater (30 grams NaCl per liter) (table 1). Breakthrough volumes increased at the higher salt concentrations, probably resulting from the so-called "salting-out effect" (Coetzee and Ritchie, 1969). On the basis of these data the SPE columns will be even more effective in collecting organic compounds in estuarine and seawater, than in typical freshwater. Andrews and Good (1982) and Hinckley and Bidleman (1989) have observed efficient isolation of pesticides from seawater with SPE columns. For freshwater samples, the breakthrough volumes of compounds with moderate capacity factors could be increased by adding large quantities of salt to induce this effect.

Changes in solution pH over the range of 2 to 8 do not seem to influence the breakthrough of DIA from the 500 mg octadecyl-silica column signficantly (table 1). The log acid dissociation constant for DIA is 1.58 (Vermeulen and others, 1982); therefore, pH effects in the range of 2 to 8 are expected to be minimal. pH has been manipulated to increase the capacity factors and breakthrough volumes for compounds with acid/base properties (Junk and Richard, 1988). The range of pH allowable for these manipulations is dictated by the analyte's hydrolysis kinetics and the dissolution of the silica.

Some investigators (Puyear and others, 1981; Andrews and Good, 1982) have suggested adding organic solvent modifiers, usually methanol, to water to increase the efficiency of the SPE column for compounds with large capacity factors. It is generally thought that the addition of methanol wets the octadecyl bonded-phase, allowing for a greater interaction with the organic chemicals in the water. The data in table 1 suggest, at least for a compound with a moderate capacity factor, the addition of methanol decreases the capacity factor and, therefore, the efficiency of the SPE column. For the typical addition of 1 percent (volume per volume) methanol, the efficiency of the SPE column is reduced by about 20 percent for DIA compared to no added methanol. The addition of an organic modifier to a water sample creates an extraction efficiency tradeoff between compounds with high and moderate capacity factors.

Breakthrough volumes were measured as a function of DIA concentration. DIA concentrations less than 1 microgram per liter gave larger capacity factors and breakthrough volumes than higher DIA concentrations (table 1). The mass of DIA retained by the SPE column at a given breakthrough percentage was also a function of influent concentration. At 100 percent breakthrough, 6.9, 65, 290, and 480 micrograms of DIA were retained on the SPE column for influent concentrations of 0.1, 1, 5, and 10 mg/L, respectively. The manufacturer (Analytichem International) suggests that the 500 mg SPE columns have a potential retention capacity of 25 mg. All of these data represent loadings which are orders of magnitude lower than the potential capacity. If breakthrough was purely a function of mass loading onto the SPE column, then the breakthrough volume would be determined by some maximum mass, regardless of volume passed through the column. On the other hand, if breakthrough were purely a function of frontal chromatography, then breakthrough should occur at a given volume, regardless of influent concentration as long as the total analyte mass on the SPE column is less than its maximum loading. Because mass loading and breakthrough volume are a function of influent, both influences are operative, but the chromatographic effect is by far the most dominant.

Table 1. *Statistical summary of breakthrough volumes at 10, 50, and 90 percent of influent concentration, capacity factor, and number of determinations for each aqueous solution tested*

[(RSD), relative standard deviation; mL, milliter; k′, capacity factor; n, number of determinations; mL/min, milliliters per minute, [MeOH], methanol concentration (volume per volume); [DIA], deisopropyl atrazine concentration; µg/mL, micrograms per milliliter; SPE, solid-phase extraction; mg, milligrams; [NaCl], sodium chloride concentration; g/L, grams per liter; ND, not determined]

	Average(RSD), breakthrough volume (mL),			Average	
	10 percent	50 percent	90 percent	k′	N
		Effect of ionic strength			
(Flow: 3 mL/min, [MeOH]: 1%, pH: 7.0, [DIA]: 1 µg/mL, SPE:500mg)					
[NaCl](g/L)					
0	51.2 (3.3)	64.7 (2.1)	89.6 (1.6)	132	5
1	51.0 (5.1)	64.7 (2.8)	85.1 (3.4)	132	4
10	54.4 (1.5)	67.1 (0.9)	90.8 (2.9)	137	3
30	68.3 (9.6)	84.0 (9.2)	114.1 (10.6)	171	3
		Effect of pH			
(Flow: 3 mL/min, [MeOH]: 1%, [NaCl]: 0, [DIA]: 1 µg/mL, SPE: 500 mg)					
pH					
2.1	55.3	69.9	ND	143	1
7	51.2 (3.3)	64.7 (2.1)	89.6 (1.6)	132	5
8	56.3	71.0	105.2	145	2
		Effect of organic modifier concentration			
(Flow: 3 mL/min, [NaCl]: 0, pH: 7.0, [DIA]: 1 µg/mL, SPE: 500 mg)					
[Methanol] (percent volume/volume)					
0	64.5 (2.5)	80.5 (3.1)	108.6 (3.7)	164	5
0.1	67.7 (5.4)	82.8 (3.9)	110.5 (4.4)	168	3
0.5	54.8 (4.9)	68.0 (3.4)	92.7 (2.3)	139	4
1	51.2 (3.3)	64.7 (2.1)	89.6 (1.6)	132	5
2	40.4 (2.5)	50.9 (1.2)	68.3 (0.9)	104	3
8	14.8 (2.4)	20.4 (0.7)	30.8 (0.2)	42	3
		Effect of analyte concentration			
(Flow: 3 mL/min, [MeOH]: 1%, [NaCl]: 0, pH: 7.0, SPE: 500 mg)					
[DIA] (µg/mL)					
0.1	53.9 (0.9)	69.0 (2.2)	106.5 (7.9)	141	3
1	51.2 (3.3)	64.7 (2.1)	89.6 (1.6)	132	5
5	48.4 (2.4)	58.8 (2.0)	78.1 (3.0)	120	3
10	40.2 (2.1)	47.9 (1.3)	55.7 (1.6)	98	3
		Effect of flow rate			
([MeOH]: 1%, [NaCl]: 0, pH: 7.0, [DIA]: 1 µg/mL, SPE: 500 mg)					
Flow Rate (mL/min)					
1	55.3 (3.7)	65.1 (4.5)	82.9 (5.4)	133	3
3	51.2 (3.3)	64.7 (2.1)	89.6 (1.6)	132	5
5	48.2	64.3	91.5	131	2
7	48.2	63.3	87.5	129	2
		Effect of SPE column size			
(Flow: 3mL/min, [MeOH]: 1%, [NaCl]: 0, pH: 7.0, [DIA]: 1 µg/mL)					
Nominal Mass of Octadecyl Packing (mg)					
100	22.7 (4.7)	29.5 (4.0)	39.8 (4.3)	94	3
500	51.2 (3.3)	64.7 (2.1)	89.6 (1.6)	132	5
5000	260.5 (5.7)	322.3 (3.6)	478.2 (1.9)	75	3

Effect of Flow Rate on Breakthrough

Flow rates of the water through the SPE columns seem to have no significant effect on the breakthrough volumes of DIA (table 1). This is in agreement with other studies (Andrews and Good, 1982; Junk and Richard, 1988). At some point, high flow rates will exceed the sorption kinetics and decrease the efficiency of the SPE columns. In practice, this is probably not a real limitation to their use.

Effect of SPE Column Size on Breakthrough

Three different size octadecyl SPE columns were tested in this study (table 1). The efficiency of the three varied in their abilities to retain the analyte. The nominal "100 mg" columns actually contained an average of 217 mg of the octadecyl packing; the nominal "500 mg" columns actually contained an average of 502 mg. Therefore, the "500 mg" columns contained only 2.3 times more packing than the "100 mg" columns. At 50-percent breakthrough for DIA, the "500 mg" column retained 2.2 times the analyte mass of the "100 mg" column, suggesting that the amount of retained analyte is proportional to the increase in the amount of packing material. Contrary to this, the "5,000 mg" columns, which contained about 10 times more octadecyl packing the "500 mg" columns, retained only 5 times (not 10 times) the analyte mass of the "500 mg" column (table 1). Because the packing material should be the same for all three columns (they all come from the same manufacturer), the differences in efficiency probably lie in the geometry of the columns and the greater possibilities for channeling in the larger columns. The length-to-diameter ratio of the column bed differed widely among the three columns.

SUMMARY

This method, which allows the real-time analysis of breakthrough of analytes from SPE columns, is useful over a wide range of solution and method variables. Each variable can be examined independently to optimize the SPE process. Breakthrough volumes can be defined more closely with this method than by typical studies with off-line analysis. This method also facilitates investigation of the sorptive mechanisms and the solution controls on these mechanisms.

The limitations of this method probably are controlled by the ultraviolet (UV) detector. All of the solutions examined in this study had concentrations at least two orders of magnitude greater than typical environmental concentrations of nanogram-per-liter to microgram-per-liter range. Unfortunately, most UV detectors cannot detect such low concentrations. This may not be a significant problem for moderately to highly water-soluble compounds (at concentrations greater than 1 mg/L) because there does not appear to be a strong dependence of the breakthrough volume on the analyte concentration. The major problem is for compounds that have very low water solubilities, where the UV-detection limit exceeds the water solubility.

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WET ATMOSPHERIC DEPOSITION OF HERBICIDES IN MINNESOTA

By Paul D. Capel[1]

ABSTRACT

Anthropogenic organic chemicals, including herbicides, can be transported long distances through the atmosphere and deposited in aquatic and terrestrial ecosystems through wet and dry processes. The herbicides, atrazine, alachlor, and cyanazine, have been detected in rain and snow during 1989 and 1990 in St. Paul and Rosemount, Minnesota. Maximum concentrations of atrazine, cyanazine, and alachlor in rain during spring were 1.6, 3.9, and 22 micrograms per liter, respectively, but decreased significantly during the following months. During one 24-hour storm in June 1990, 43 sequential samples were collected. Maximum concentration of all three herbicides was present in the first millimeter of rain. Atrazine and alachlor were detected throughout most of the event, but cyanazine was detected in only the first three samples (about 4 millimeters of rain). Yearly fluxes of the three herbicides, alachlor, atrazine, and cyanazine, to the State of Minnesota are estimated to 40, 20, 20 megagrams per year, respectively. Although this is less than 1 percent of their total agricultural application in Minnesota, the atmospherically deposited atrazine potentially could have a harmful effect on aquatic and terrestrial ecosystems.

INTRODUCTION

Many anthropogenic organic chemicals are transported long distances through the atmosphere and deposited in aquatic and terrestrial ecosystems through wet and dry processes (fig. 1). Organic chemicals entering the environment are distributed between various environmental compartments (biota, soil, surface water, ground water, and atmosphere) according to their physical and chemical properties (such as water solubility, vapor pressure, and acid dissociation constant) and environmental conditions (such as temperature, windspeed, and water movement). Introduction of organic chemicals into the atmosphere can either be through the vapor phase or through the particulate phase. Once in the atmosphere, the chemicals can be transported, chemically transformed, deposited, or accumulated. Deposition can be either by wet mechanisms, such as rain and snow, or by dry mechanisms, such as dust fallout, fog, or air-water exchange.

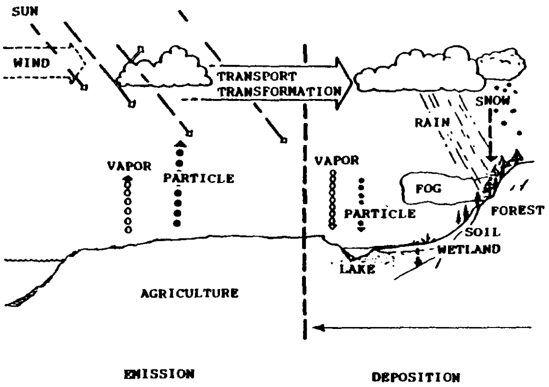

Figure 1. Atmospheric cycling of agricultural chemicals.

Previous studies have shown that many agricultural organic compounds, both herbicides and insecticides, are observed in the atmosphere (Eisenreich and others, 1981; Rice and others, 1986; Bidleman and others, 1987, 1989; Glotfelty and others, 1987, 1991; Richards and others, 1987; Shulters and others, 1987; and Leuenberger and others, 1988). These include many of the organochlorine insecticides (DDT, lindane, toxaphene, chlordane, endosulfan, and heptachlor), organophosphate insecticides (diazinon, parathion, chloropyrifos, methidathion, malathion, fonofos, dimethoate), and two carbamate insecticides (carbofuran, carbaryl). The herbicides that have been observed in the atmosphere include acid amides (alachlor, metolachlor); triazines (atrazine, cyanazine, simazine, metribuzin); phenols (DNOC, dinoseb); thiocarbamates (EPTC, butylate); and a phenoxy acid (2,4-D). These chemicals have been observed in the atmospheric vapor phase or in precipitation (rain, snow, fog).

Herbicides can be introduced into the atmosphere as vapors or associated with particles. Volatilization during application or from soil particles results in vapor-phase chemicals in the air. Glotfelty and others (1989) and Taylor and Glotfelty (1989) have reported that about 26 percent of alachlor and 2 percent of atrazine are lost from the field by volatilization during the first 24 days after application. Windblown dust introduces the pesticides to the atmosphere in the particulate form (fig. 1). Regardless of how a herbicide is introduced to the atmosphere, it will be distributed between the vapor and particulate phases according to its vapor pressure, the air temperature, and the nature and concentration of the airborne particles. Distribution of the herbicides between the vapor and particulate phases determines the operative mechanism(s) for its removal from the atmosphere. Chemicals in the vapor phase can be removed by air-water exchange with surface water and falling precipitation droplets. Chemicals in the particulate phase can be removed by dry deposition (dustfall) and particle scavenging by falling precipitation droplets (fig. 1). The overall importance of the emission and deposition mechanisms of highly water-soluble herbicides to and from the atmosphere is relatively unknown.

This paper summarizes preliminary results of an ongoing study of the emission, transport, and depositional mechanisms of herbicides in the atmosphere. The focus of the study is on the high-use pesticides in the corn and soybean production areas of the midcontinental United States, including atrazine, alachlor, cyanazine, and carbofuran. The paper is limited to the discussion of the data for atrazine, alachlor, and cyanazine in wet deposition during the first year of the study.

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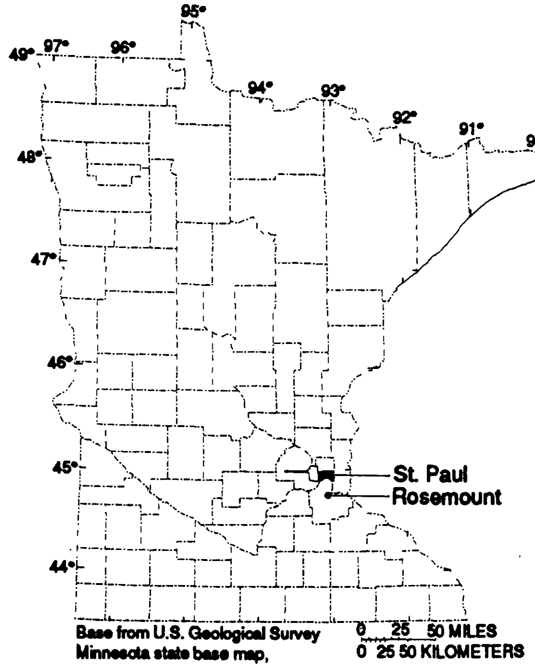
METHODS

Sampling

Rain samples were collected in the urban area of St. Paul, Minn., from March through November 1988, and from March through April 1990. In late April 1990, the sampling site was moved to the University of Minnesota's Agricultural Experiment Station in Rosemount, Minn.--an intensively farmed area about 30 miles south of St. Paul (fig. 2). Rain samples were collected on an event basis by the wet-only sampler, which is traditionally used by the National Atmospheric Deposition Program. To decrease the possibility for contamination, the wet-only rain sampler was modified by inserting a Teflon[2]-lined pot in the plastic collection bucket. Snow samples were collected from the St. Paul site on an event basis. Snow was collected from a cleaned Plexiglas sheet with a 10-cm (centimeter) internal-diameter glass tube and 20-cm x 25-cm glass sheet.

During one 24-hour storm event in June 1990 in St. Paul, 43 consecutive samples were collected. The rain was collected on a cleaned 1 square-meter aluminum funnel. This was a different sampler than the one described above. The sampling frequency was based on volume rather than time. Some samples collected during intense rain represent less than 1 minute of rainfall; some samples collected during light rain represent many hours of rainfall. Each of the 43 samples consisted of a 1-liter filtered aliquot analyzed for herbicides and dissolved organic carbon, followed by two 60-mL (milliliters) filtered aliquots analyzed for nutrients and major ions. Specific conductance and pH were measured from the herbicide sample.



Base from U.S. Geological Survey
Minnesota state base map,
1:1,000,000,1965

Figure 2. Sampling sites in St. Paul and Rosemount, Minnesota.

Analysis

The herbicides in rain and snow samples were isolated by 500 milligrams octadecyl solid-phase extraction (SPE) columns after the addition of 1 percent (volume per volume) methanol and two analytical surrogates: terbuthylazine and butachlor. The SPE columns were cleaned and activated by passing 10 mL of diethyl ether, 10 mL methanol, and 5 mL "organic-free" deionized water through them. The preweighed water sample was passed through the SPE column under a vacuum. The herbicides were removed from the SPE column, after centrifugation to remove the residual water, by elution with 2 mL diethyl ether. The diethyl ether extract was dried on an anhydrous sodium sulfate column and reduced to about 100 microliters by a gentle stream of purified nitrogen. d_{10}-anthracene and 4,4'-dibromobiphenyl (500 nanograms each) were added as internal standards just before analysis. Final analysis was performed on a 30-meter, 5-percent phenyl-methyl capillary gas chromatographic column. Detection was by a mass selective detector (Schlotter and others, 1991).

RESULTS AND DISCUSSION

Seasonal Changes in Herbicide Concentrations in Rain and Snow

Each of the three herbicides (atrazine, alachlor, and cyanazine) quantified in rain and snow had definite seasonal concentration cycles (fig. 3). All three had maximum rain concentration during the spring of each year, immediately following application. Their concentrations decreased within weeks of application. Alachlor and cyanazine in rain were at concentrations below the detection limit for most rain events after July. Atrazine was detected in most rain events and many snow events throughout the year. This reflects the longer environmental residence time of atrazine, compared to alachlor and cyanazine. The presence of atrazine in snow, even when snow covers the ground locally, suggests either that its atmospheric residence time is long or that there is a continual atmospheric source with long-range atmospheric transport. It is possible that both are true.

Alachlor is the most heavily used herbicide in the midcontinental United States (Burkart and others, 1988); it volatilizes from soil to a greater extent than does atrazine or cyanazine (Taylor and Glotfelty, 1989). The alachlor concentration in one rain during late May 1990 was 22 µg/L (micrograms per liter) (fig.3)--the overall highest concentration of any of the herbicides quantified in this study. This concentration is four times the U.S. Environmental

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[2] The use of brand, firm, or trade names in this paper is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

Protection Agency's drinking-water regulation for alachlor. Generally, concentrations of alachlor in the spring were 1 to 2 µg/L (fig. 3).

Atrazine is the second most widely used herbicide in the midcontinental United States (Burkart and others, 1988). Its concentrations in spring rain were generally 0.5 to 1.5 µg/L (fig. 3). Its concentrations in snow were in the range of less than 0.02 to 0.03 µg/L (fig. 3).

Cyanazine is used to a far lesser extent than either alachlor or atrazine (Burkart and others, 1988). It is reported as having the extremely small vapor pressure of 200 nanoPascals at 20 degrees Celsius (Worthing, 1988), and, therefore, volatilization should be minimal. The presence of cyanazine in the atmosphere suggests that wind-blown soil particles may be the source, but this is speculative. Springtime concentration maximums for cyanazine were generally 2 to 4 µg/L, which is surprising given the low application and extremely low vapor pressure of this compound. The length of time that cyanazine appears in rain is shorter than that of the other two herbicides, but it was detected twice in rain and snow during the autumn (fig. 3).

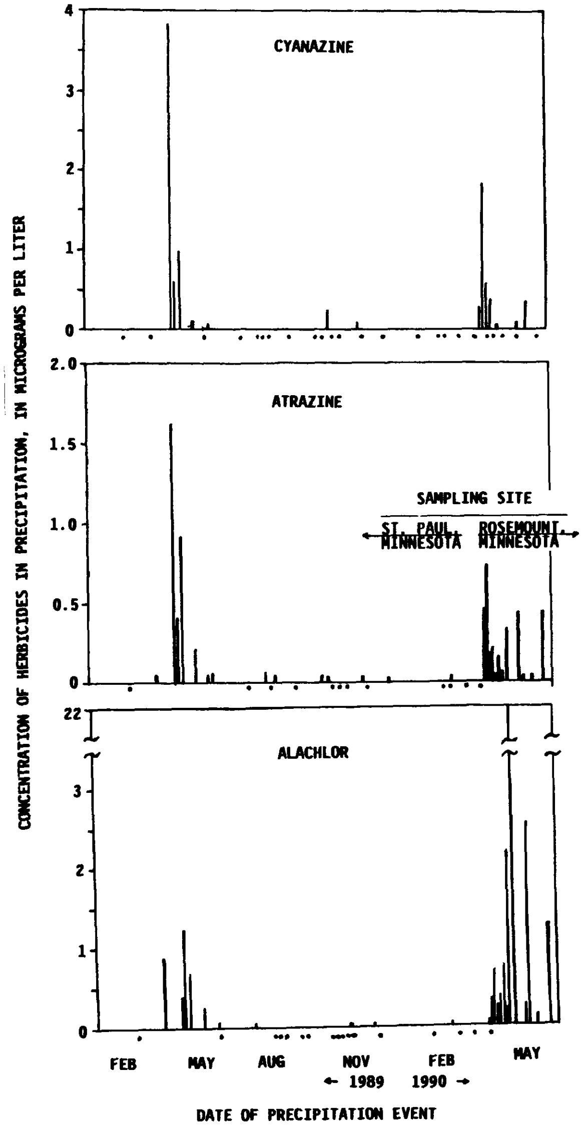

Figure 3. Concentrations of three herbicides (atrazine, alachlor and cyanazine) during rain and snow events, March 1989 through June 1990, in St. Paul and Rosemount, Minnesota. The dots below each of the graphs represent rain or snow events in which the herbicide was not detected.

Removal of Herbicides from the Atmosphere During a Single Rain Event

During a single 24-hour rainfall (50 mm (millimeters) of rain) in June 1990, 43 consecutive samples were collected and analyzed for herbicides (fig. 4). Different atmospheric washout patterns were observed among the three herbicides. Cyanazine had an initial concentration of 2 µg/L and decreased to below the detection limit (20 µg/L) after the first 4 mm of rain (three samples). It was detected in only two other samples during the storm.

The concentration of atrazine, which was initially 2 µg/L, decreased quickly in the first four samples. The rain intensity slowed during collection of samples 6 through 8. The rain ceased for 20 minutes after sample 8 was collected. (Total rainfall for samples 1 through 8 was about 12 mm.) The concentration of atrazine increased in the first sample (number 9) after the pause, then decreased thereafter, to below the detection limit (20 µg/L). In the second-half of the rain event, atrazine was detected at slowly increasing concentrations (fig. 4).

The washout pattern for alachlor was similar to that of atrazine, but some differences were noted. The initial concentration of 3.5 µg/L for alachlor decreased in the first 4 mm of rain (three samples), but then increased to about one-half its initial concentration in sample 7. The second peak of alachlor preceded the second peak of atrazine and the pause in the storm. The concentration of alachlor declined through the rest of the storm, but it was detected in every sample, although at low concentrations. As occurred with atrazine, the concentration of alachlor steadily increased, during the second-half of the the rain event. The concentration of alachlor was always greater than that of atrazine during this storm.

The three washout patterns may give insight into how the herbicides are removed from the atmosphere, but final interpretation must consider their concentrations in the particulate phase, which was collected but has not yet been analyzed. These washout patterns show that initial herbicide concentrations in rain are much higher than their final concentrations measured at the end of the storm. The effect of these initially short-term, high herbicide concentrations in rain on aquatic and terrestrial ecosystems are unknown.

Fluxes of Herbicides in Wet Deposition and their Significance

Yearly fluxes of herbicides in wet deposition (rain and snow) can be estimated. The estimated fluxes are 1 to 6 (g/ha)/yr (grams per hectare per year) for alachlor and 0.5 to 3 (g/ha)/yr for atrazine and cyanazine. The ranges in atmospheric fluxes represent differences in average rainfall throughout Minnesota. These fluxes total to about 40, 20, and 20 megagrams of alachlor, atrazine, and cyanazine, respectively. Although this represents less than 1 percent of total application in Minnesota, it nonetheless is an appreciable amount.

The environmental effect of the herbicides deposited by rain is largely unknown. The chemicals are introduced into ecosystems for which they were not intended. Fortunately, the herbicides do not have significant toxicity to fauna and do not bioaccumulate to an appreciable extent. Their potential harm to an ecosystem lie in their herbicidal properties. At some concentration level, they can act as herbicides to aquatic and terrestrial flora. Whether the amounts contributed to these ecosystems from atmospheric deposition will ever reach toxic levels is unknown at this time.

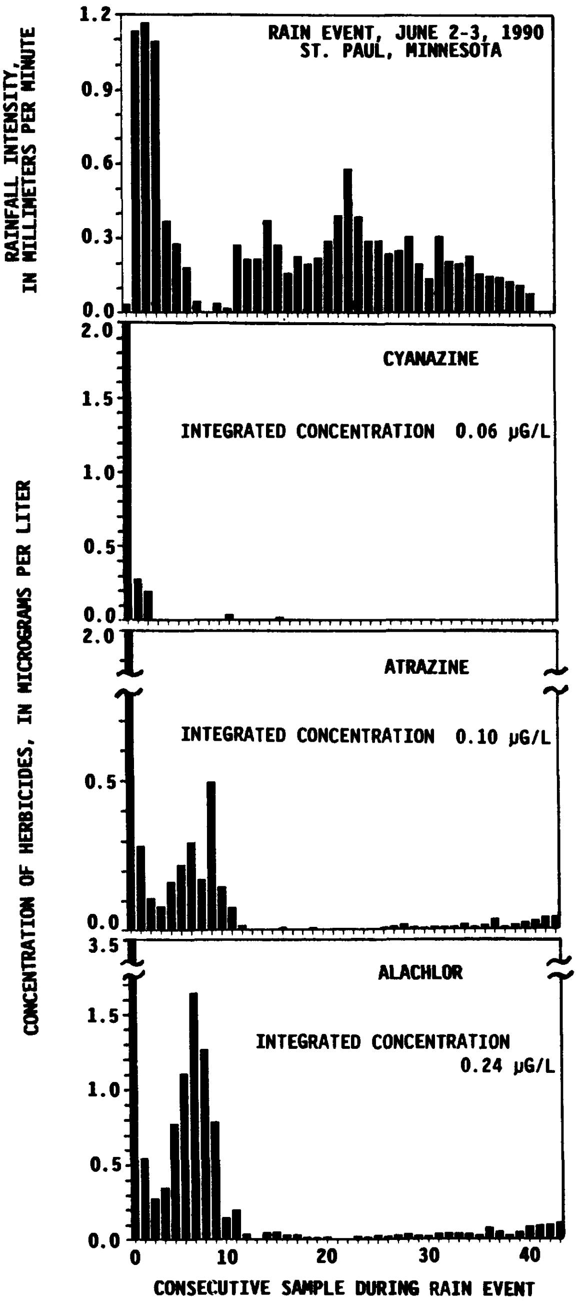

Figure 4. Rainfall intensity and concentrations of atrazine, alachlor, and cyanazine during a single 24-hour rain event, June 1990, St. Paul, Minnesota.

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RELATIONS BETWEEN WATER DISCHARGE AND HERBICIDE CONCENTRATION IN THE MINNESOTA RIVER, MINNESOTA

By Shawn P. Schottler[1], Steven J. Eisenreich[1], *and* Paul D. Capel[2]

ABSTRACT

The hydrologic and chemical controls on the concentration, sources, and fate of atrazine, alachlor, and cyanazine in the Minnesota River are being investigated. The Minnesota River drains a large agricultural watershed (41,500 square kilometers) in south-central Minnesota where application of atrazine, alachlor, and cyanazine is estimated to be 700, 1,800, and 550 megagrams of active ingredient, respectively. Water samples are collected 3 days a week at Mankato, Minn., and analyzed for atrazine, deethyl atrazine, deisopropyl atrazine, alachlor, demethylmethoxy alachlor, and cyanazine. The herbicides were isolated by octadecyl solid-phase extraction and analyzed by capillary gas chromatography with a mass-selective detector. Data presented here are for the parent herbicides only (atrazine, alachlor, and cyanazine) for the period spring through autumn 1990. During this time, the herbicide concentrations ranged from less than 30 nanograms per liter to greater than 2,500 nanograms per liter. The presence and variability in concentration of each of the herbicides is interpreted considering hydrologic conditions such as discharge and rainfall and herbicide properties such as application period, water solubility, and environmental half-life. Daily and annual fluxes are calculated for each of the three herbicides in the Minnesota River for 1990. The annual fluxes of these three herbicides account for less than 1 percent of their total application in the watershed.

INTRODUCTION

The presence of agricultural chemicals in ground water and surface water threatens a valuable natural resource (Cohen and others, 1984; Klaseus and others, 1988; Pionke and others, 1988). The Midwestern United States is a region of intense agricultural activity where millions of kilograms of active pesticidal ingredients are applied annually. Although only a very small percentage of applied chemicals reaches the ground water or surface waters (Pereira and Rostad, 1990), concentrations occasionally reach levels that threaten nontarget aquatic organisms or potentially affect human health. Central issues in assessing the effect of agrichemicals on the environment are quantifying their transport in runoff and ground water to surface waters, determining their seasonal flux (load) in the river, and elucidating their environmental fate.

Agrichemicals applied to croplands can undergo physical, chemical, and biological processing. Depending on the herbicide's properties, and on environmental conditions such as wind, temperature, soil moisture, soil type, and soil organic matter, a herbicide may be transported through the soil column, sorb to soil particles, undergo chemical and biological transformations, or volatilize to the atmosphere (Biggar and Seiber, 1987). The efficiency and specific mechanisms of environmental processes govern the availability of the herbicide to be transported to surface waters. Transport to the river can be by tributary flow, through ground-water discharge, and from atmospheric deposition. Transport away from the watershed occurs through discharge, volatilization, and ground-water recharge. A herbicide may also experience losses within the surface-water system itself. Internal cycling processes include sorpt to particulates, sedimentation and resuspension, and chemical and biological transformation. The dissolved concentration of a herbicide in a river can be regarded as a summation of all the inputs, outputs, and internal cycling processes.

This paper describes the results of the first 6 months of study on the transport, fluxes,and fate of high-use herbicides (atrazine, alachlor, and cyanazine) in a major agricultural watershed. Environmental responses and processing of the three herbicides have been examined with respect to hydrologic and chemical controls.

Alachlor and atrazine are the most heavily used agrichemicals in the United States and Minnesota. Annual application in the Minnesota River watershed for the herbicides are given in table 1. Alachlor is a preemergent herbicide used on corn and soybeans. Atrazine and cyanazine

Table 1. *Water solubilities, detection ions, and estimated fluxes in the Minnesota River of atrazine, alachlor, and cyanazine*

[mg/L, milligrams per liter; °C, degrees Celsius; m/z, mass to charge ratio; kg/d, kilograms per day; Mg, megagrams]

	Atrazine	Alachlor	Cyanazine
Water solubility, mg/L at 25°C	33[1]	148[1]	171[2]
Detection ion, m/z	200	160	225
Confirmation ion, m/z	215	188	240
Estimated application of active ingredient in the Minnesota River watershed in 1989, Mg	700	1,800	550
Average daily flux, May to June, 1990, kg/d	14	10	14
Estimated total annual flux in the Minnesota River in 1990, Mg	1.1	.5	1.3
Percentage of herbicide applied in the watershed which entered the Minnesota River	.15	.025	.25

[1] Suntio and others, 1988

[2] Windholz and Budavari, 1983

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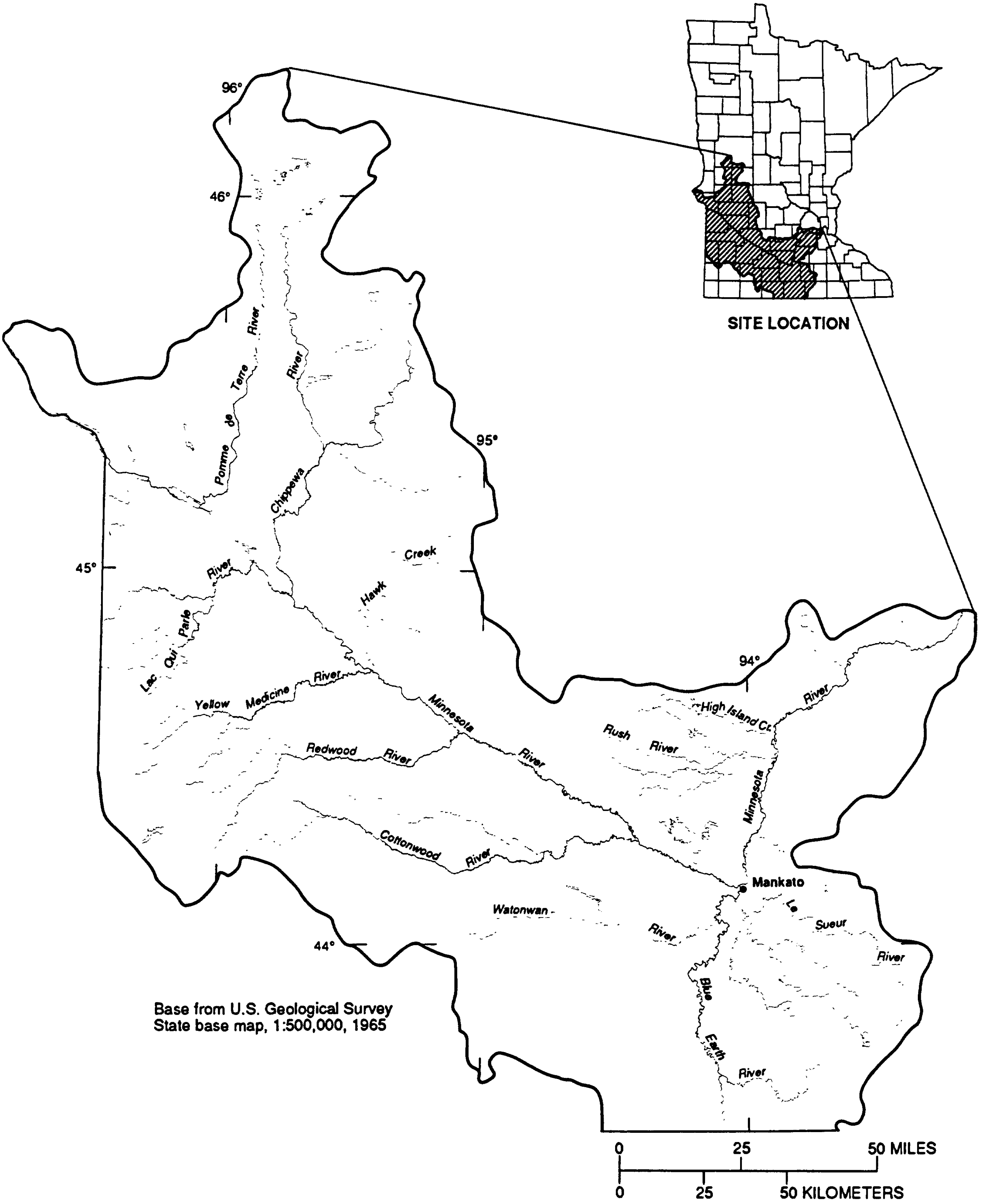
[2] U.S. Geological Survey, St. Paul, Minn.

are preemergent and postemergent herbicides used on corn. Their application to soil is seasonal and usually by surface spraying. These herbicides are highly water soluble (table 1) ranging from 33 mg/L (milligrams per liter) for atrazine to 171 mg/L for cyanazine (at 20°C). As a result of these high water solubilities, these herbicides can exhibit significant mobility in the soil columns and surface runoff (Rao and others, 1980).

The Minnesota River drains approximately 41,500 square kilometers in south-central Minnesota and flows northwest to southeast (fig. 1). Discharge of the river ranges from 5 to 40 million m^3/d (cubic meters per day) in


SITE LOCATION
96°
46°
45°
95°
94°
44°
Pomme de Terre River
Chippewa River
Hawk Creek
Lac Qui Parle River
Yellow Medicine River
Redwood River
Minnesota River
Cottonwood River
High Island Cr.
Rush River
Minnesota River
Mankato
Watonwan River
Le Sueur River
Blue Earth River
0 25 50 MILES
0 25 50 KILOMETERS

Base from U.S. Geological Survey State base map, 1:500,000, 1965

Figure 1. Minnesota River Basin.

spring and summer with a winter base flow of about 0.3 to 1 million m^3/d. Soils in the watershed are typically fine or loamy textured overlying loamy calcareous subsoil with poor to moderate drainage. The entire basin is intensively row-cropped and many of the fields are tiled or landscaped to enhance drainage.

METHODS

Water samples were collected on alternate days in conjunction with daily sediment sampling by the U.S. Geological Survey of the Minnesota River just downstream of Mankato, Minn. (fig. 1). Depth integrated samples are collected with a D-74 sampler from a bridge over the river. About 500 mL (milliliters) are collected and kept in cool (<4°C) (degrees Celsius) dark storage until extraction within a few days. The samples are filtered through 90 mm (millimeter) glass-fiber filters and the particulate matter saved for future analysis. Terbutylzine and butachlor are added to 350 mL of the filtrate as analytical surrogates. The herbicides were isolated from this filtrate by passage through a 5 g (gram) octadecyl-bonded silica solid-phase extraction (SPE) column. One percent methanol (volume per volume) is added to the sample to enhance SPE efficiency. The 5 g SPE column is precleaned with 8 mL of diethyl ether, conditioned with 6 mL methanol, and flushed with organic free distilled water. The sample is drawn through the SPE column under gentle vacuum to produce a flow rate no greater than 10 mL per minute.

The SPE column was then eluted with 15 mL diethyl ether and the extract is passed through 25 milligrams of anhydrous sodium sulfate to remove excess water. The extract was reduced to 50 microliters with a slow steady stream of nitrogen. Five hundred nanograms of d_{10}-anthracene and 4,4′-dibromobiphenyl were added as internal standards. Final analysis was performed by capillary gas chromatography and mass-selective detection. Single ion monitoring mode was used with at least one confirmation ion (table 1). Sample injection was at 60°C. After 1 minute at this temperature, the column was ramped to 140°C at a rate of 20°C/min (degrees Celsius per minute), a final temperature of 280° was reached by a second ramp of 10°C/min. Detection temperature as set at 250°C. The capillary gas chromatography column is a 30-meter, 5-percent phenylmethyl bonded phase glass capillary column, 0.32mm internal diameter. Helium is used as the carrier gas. For a 350 mL water sample, the reporting limit is 30 ng/L (nanogram per liter). Recoveries of analytical surrogates are 90 ±20 percent. None of the herbicides have been detected in any of the procedural blanks.

RESULTS AND DISCUSSION

Measurements of atrazine concentration show that it is highly related to application period, discharge, and rainfall. Atrazine concentrations do not exceed values over a few hundred nanograms per liter until the first significant discharge events following the application period (fig. 2A). The atrazine concentration peaked on June 14, 11 days before the largest water discharge peak. The June 14 peak of atrazine corresponds to a precipitation event that totaled about 3 inches for most of the Minnesota River watershed over the period June 12-16. The water discharge peak was generated by this precipitation event and a smaller event that occurred on June 20. The peaking of atrazine concentration prior to the peaking of discharge probably results from the hydrophilic nature of atrazine and hence its availability to runoff generated by the first rainfall following application. Atrazine concentration declines progressively from mid-June through August and, by the end of August, has reached spring flow concentrations (fig. 2A) reflecting the efficiency of atrazine removal from the cropland.

Streamflows in the river during March and early April show base flow discharge conditions for the Minnesota River. Because there are no other major surface water inputs during this time, this flow is almost entirely due to ground-water discharge. Thus, atrazine concentrations detected during this flow period likely represent atrazine present in the surficial aquifer ground water recharging the river. The first small peak of atrazine in late March shows the flushing of atrazine with snowmelt and the first precipitation event. (The winter of 1989-90 had a minimal snowmelt.) Atrazine in this overland flow is likely from residual atrazine from packed snow and windblown soil accumulated in ditches and small drainages during the winter.

Alachlor shows a similar relation to application and discharge (fig. 2B) as that of atrazine. Alachlor has a longer and earlier application period than atrazine. It is many times more water soluble, has a shorter environmental half-life (Hartley and Kidd, 1983), and more of it is applied each year than atrazine (table 1). These properties may account for the slightly different response of alachlor to river discharge. Alachlor shows an extended period of moderately high concentrations (300-600 ng/L) starting in early spring. These concentrations peak with the intense application period and increasing discharge. Because of its high water solubility, alachlor is easily transported through surface runoff and its concentration peaks before major discharge peaks.

Alachlor concentrations drop quickly (as compared to atrazine) to very low values in early summer and to less than its detection limit by early fall. Alachlor, because of its solubility and relatively short environmental half-life, seems to be almost completely removed from the system by fall and, therefore, is not present in detectable amounts in the first spring runoff or base flow.

Cyanazine is often applied as a rescue treatment (a followup to unsuccessful herbicide applications) and, therefore, cannot be assigned a specific application period. It is also not used in quantities as great as those used for atrazine and alachlor. Cyanazine is also the most water soluble (table 1) and has the shortest environmental half-life (Hartley and Kidd, 1983) of the three herbicides reported here. It is likely that because of these factors, cyanazine's concentration curve appears somewhat different from those of atrazine and alachlor.

The dates when the concentration peaks for the different herbicides, at the sampling point on the river, is a complex function of many factors. Distance of herbicide runoff upstream from the sampling point, relations between application rates and rainfall intensity at various locations in the basin, and different chemical properties of the herbicides produce a temporal variation in the peak herbicide concentration at the sampling point. Cyanazine, however, due to its higher water solubility, and varied application practices has numerous peaks in concentration which may represent washout from localized areas at varying distances upstream.

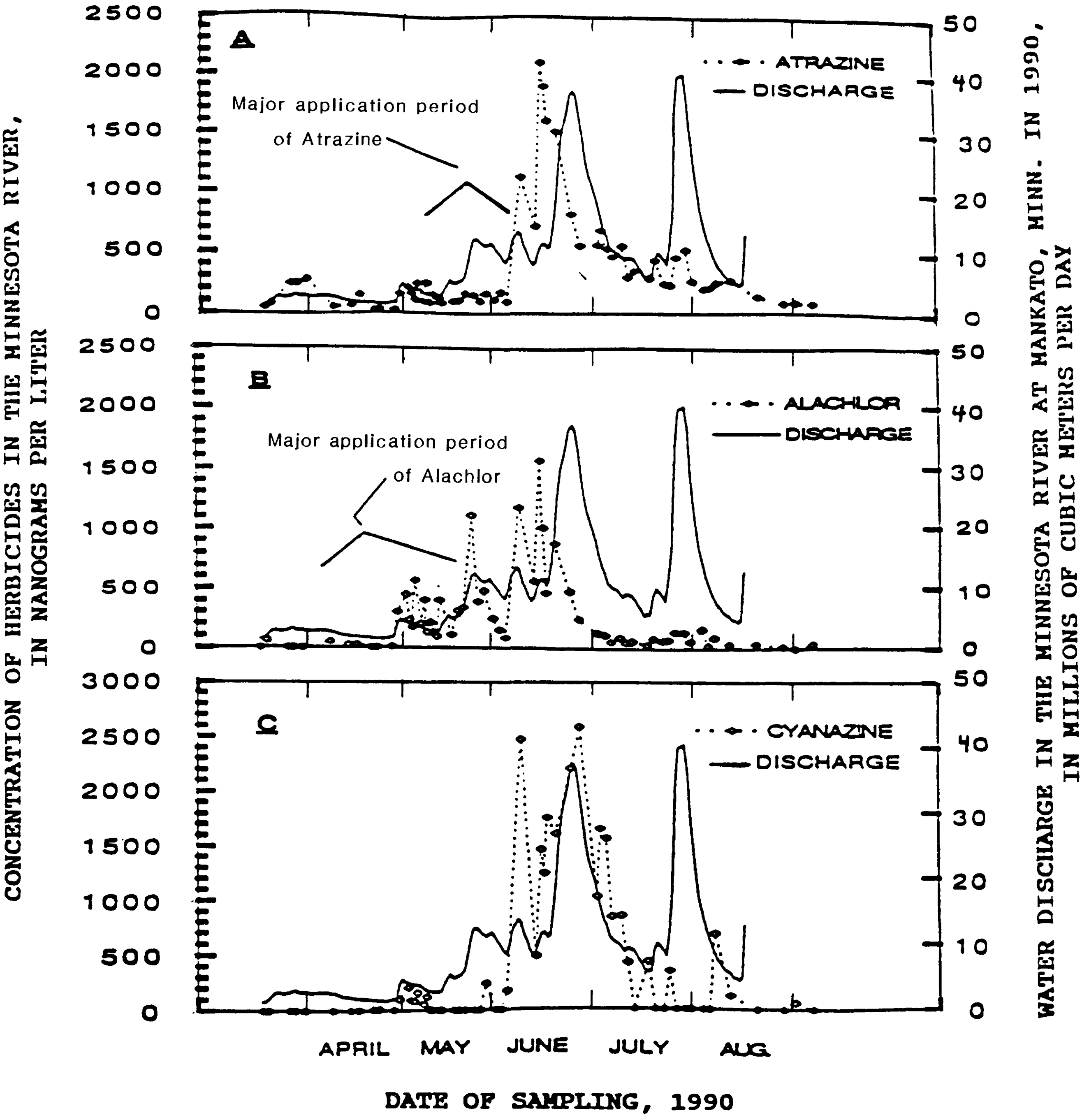


Figure 2. Water discharge and concentrations of atrazine, alachlor, and cyanazine in the Minnesota River at Mankato, Minnesota, for the period April through August 1990.

Using daily concentrations and daily mean discharge, it is possible to construct an estimate of the daily flux of each herbicide. The daily and annual loadings for the three herbicides are similar. Daily load reaches a maximum during high-flow periods after application. The magnitude and length of these maximums vary in the same fashion as their daily concentrations. Maximum alachlor loading occurs over a broad period (about 40 days) with daily loads <20 kg/d (kilograms per day). Cyanazine's daily load peaks sharply over a short period (about 15 days) and reaches a maximum of about 85 kg/d (fig. 3). Atrazine maximum loading falls between that of alachlor and cyanazine, but because of its longer environmental half-life, it peaks again following heavy rains in late summer (fig. 3).

By summing the measured daily fluxes, and extrapolating for autumn and winter, yearly loading of the three herbicides have been estimated. The total masses of cyanazine and atrazine passing the sampling site are slightly greater than 1 megagram each per year, and that of alachlor is about one-half of this (table 1). If yearly loading is compared to the total amount of each herbicide applied in the watershed, it is apparent that only a very small percentage (less than 1 percent) (table 1) of the mass applied is transported to the Minnesota River.

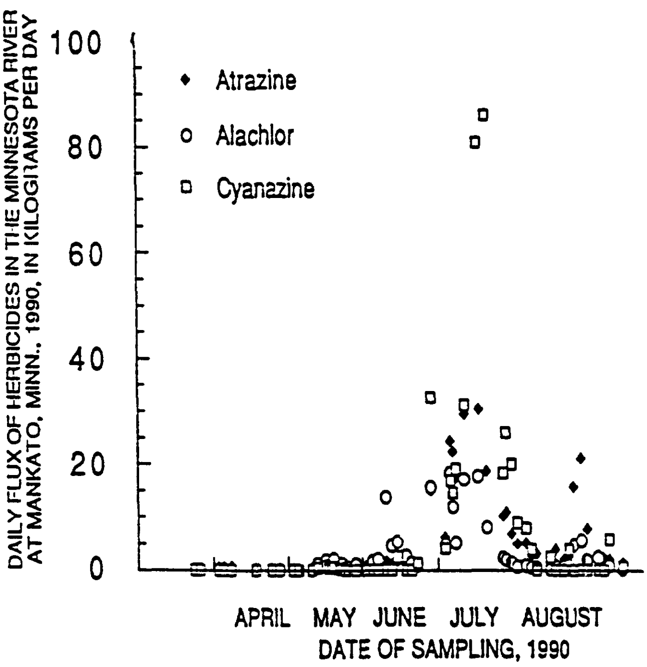


Figure 3. Daily flux of atrazine, alachlor, and cyanazine in the Minnesota River past Mankato, Minnesota, for the period April through August 1990.

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TRIAZINE HERBICIDES IN SELECTED STREAMS IN ILLINOIS DURING STORM EVENTS, SPRING 1990

By Richard H. Coupe[1] and Gary P. Johnson[1]

ABSTRACT

A reconnaissance for triazine herbicides in surface waters of the Midwestern United States showed that large concentrations of herbicides in surface water can occur following the first runoff event after the application of herbicides to the fields. In the spring of 1990, automatic samplers were installed to collect surface-water samples at three sites in Illinois. The samples were used to quantify the magnitude and duration of the concentration of triazine herbicides following their application.

A major storm in mid-May 1990 produced runoff affecting all three sites. Silver Creek near Freeburg had a record peak discharge of 11,000 cubic feet per second on May 17; the recurrence interval of this discharge event was 10 years. The recurrence interval of the event in the Sangamon and the Iroquois Rivers was 5 and less than 2 years, respectively.

In the Silver Creek basin, triazine-herbicide concentrations increased sharply during even small storms, reaching a peak of 32 micrograms per liter several days before the peak discharge. A different pattern was noted for the Sangamon River where concentrations of triazines did not change rapidly and did not reach the concentrations measured in Silver Creek. The peak concentration of 14 micrograms per liter was reached several days after the peak discharge. The Iroquois River near Chebanse had a peak triazine concentration of 37 micrograms per liter on May 13, 2 days before the peak discharge. On May 19, another storm in the Iroquois River drainage basin produced a peak discharge of 7,380 cubic feet per second; the peak triazine concentration associated with this event reached 13 micrograms per liter on the next day.

INTRODUCTION

In May and June of 1989, a reconnaissance for triazine herbicides in surface waters of the Midwest was conducted by the U.S. Geological Survey (USGS). Water samples were collected at 132 sites in 10 States during the first runoff event following application of the herbicides; 26 of those sites were in Illinois. Results from this reconnaissance indicated that the triazine herbicide atrazine, was detected at 98 percent of the sites in the study area (Goolsby and Thurman, in press), and that atrazine concentrations exceeded the U.S. Environmental Protection Agency's Proposed Maximum Contaminant Level of 3 μg/L (micrograms per liter) 50 percent of the time in the surface waters at these sites. Questions raised as a result of this initial reconnaissance included (1) what quantity of herbicides is being transported into the surface waters during the first storm event following the application of herbicides, and (2) how long do high herbicides concentrations persist in the streams, following this first event?

The USGS in Illinois, as part of the USGS Toxic Substances Hydrology Program, and in cooperation with the Illinois Environmental Protection Agency (IEPA), installed automatic samplers in three watersheds in Illinois. This paper describes the magnitude and duration of concentrations of triazine herbicides at the three sites during the first runoff event following the application of herbicides in 1990.

The three sites in this study--Silver Creek near Freeburg (05594800), Sangamon River at Monticello (05572000), and Iroquois River near Chebanse (05526000)--were selected to represent different areas of the State (fig. 1) and different size drainage basins (table 1). These sites also were selected because the predominant land use is agriculture with a crop rotation of corn and soybean. No major metropolitan or industrial areas are located within these drainage basins.

METHODS

Automatic samplers were used to collect samples from the streams for herbicide analysis. Baker and Richards (1989) showed that herbicide concentrations in surface water are relatively constant during steady-flow periods, but that concentrations can change rapidly during storm runoff. Therefore, base flow samples were collected every 48 hours. As the stage increased above a preset stage, the frequency of sample collection was increased to either three or four times a day, depending on the site. In addition to the three or four samples collected daily, if a rise or fall in stage per unit time was greater than a preset level, a sample was collected. The samplers were operated from mid-April until late August 1990.

The automatic sampler was modified by replacing the existing silicone tubing with Teflon[2] tubing; a small section of silicone tubing was needed for the peristaltic pump. Samples were collected in clean 350 milliliter glass bottles. The bottles were capped with aluminum foil and transported back to the office for processing. The bottles were collected from each site at least twice weekly and more often during storms. Water for triazine analyses was passed through a glass-fiber filter. The triazine analyses were performed by the USGS office in Lawrence, Kans.

All samples were analyzed for triazine herbicides by a modification of the immunoassay method described in Goolsby and others (1991). This analysis is very sensitive to atrazine but also responds, to a lesser degree, to propazine and simazine. Although the immunoassay test does not yield specific concentrations of individual compounds, it is very useful as a screening/reconnaissance tool. It gives reliable semi-quantitative results, it is inexpensive, and it is quick.

WEATHER AND CROP CONDITIONS

Although precipitation during April 1990 was below normal, wet conditions during March caused April soil

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[1] US Geological Survey, Urbana, Ill.

[2] Use of brand names in this paper is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

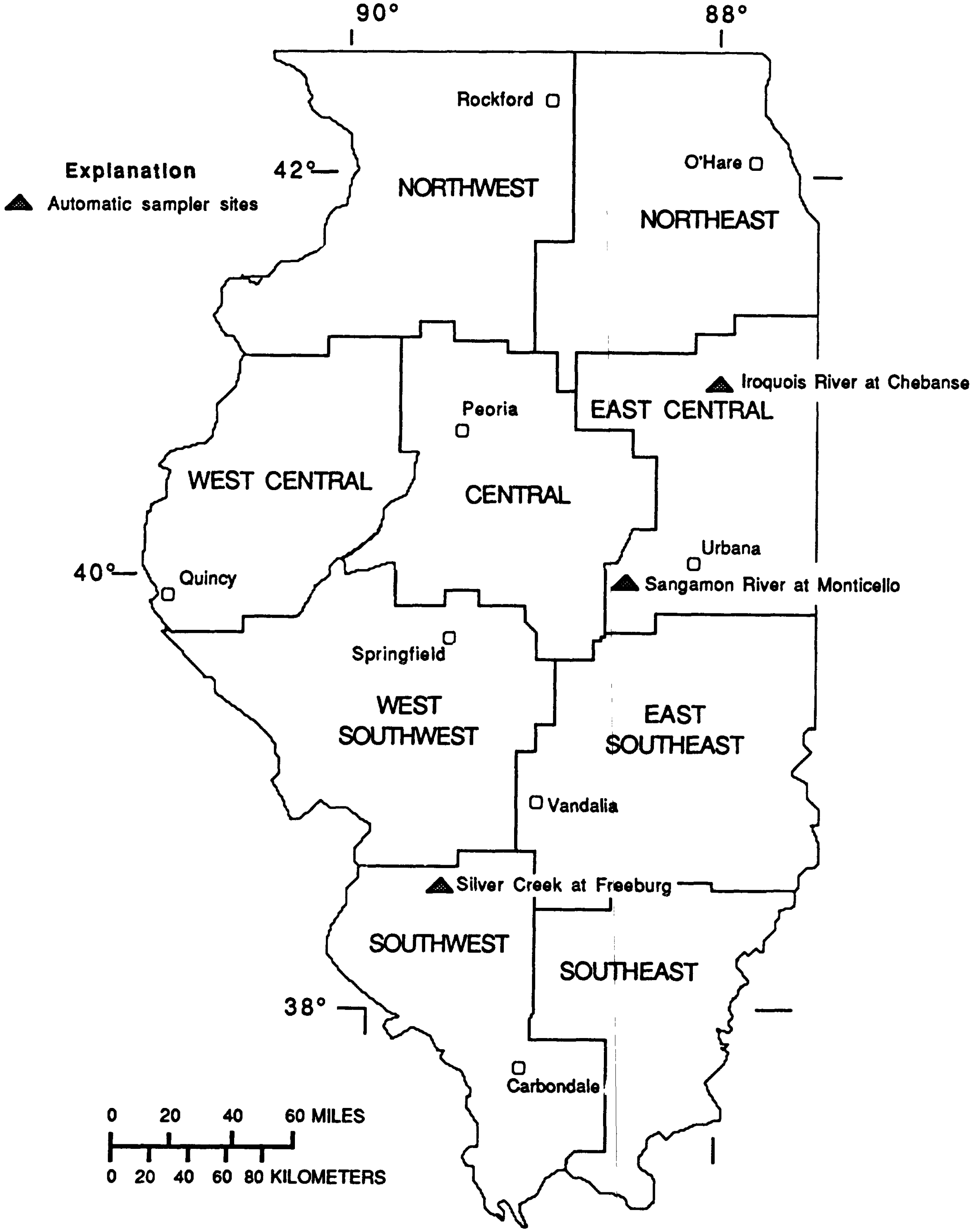
90°
88°
42°
40°
38°
Explanation
▲ Automatic sampler sites
Rockford
O'Hare
NORTHWEST
NORTHEAST
Iroquois River at Chebanse
Peoria
EAST CENTRAL
WEST CENTRAL
CENTRAL
Urbana
Quincy
Sangamon River at Monticello
Springfield
WEST SOUTHWEST
EAST SOUTHEAST
Vandalia
Silver Creek at Freeburg
SOUTHWEST
SOUTHEAST
Carbondale
0 20 40 60 MILES
0 20 40 60 80 KILOMETERS

Figure 1. Crop reporting district and automatic sampler sites in Illinois.

Table 1. *Description of the study sites*

Station number	Station name	Period of record	Area of drainage basin (square miles)	Average discharge (cubic feet per second)
05594800	Silver Creek near Freeburg	1970-89	464	350
05572000	Sangamon River at Monticello	1914-89	550	403
05526000	Iroquois River near Chebanse	1923-89	2,091	1,655

moisture conditions throughout the State to exceed average April soil-moisture during the previous 5 years (Semonin, 1990a, 1990b). Herbicides were applied to cropland prior to or during planting within about a 1-month period from late April through late May. By April 30, only 21 percent of the corn crop throughout the State had been planted, as compared to the 5-year average of 40 percent (Illinois Agricultural Statistics Service, 1990a).

In the East-Central crop reporting district (CRD), which includes parts of the Iroquois River and Sangamon River drainage basins (fig. 1), 90 percent of the corn was planted by May 13 (Illinois Agricultural Statistics Service, 1990b); 60 percent of the corn was planted after April 30. In the Silver Creek drainage basin, which is in the West Southwest and Southwest CRDs (fig. 1), wet soil conditions kept planting behind schedule. As of April 30, 30 percent of the corn had been planted in the West Southwest CRD and 10 percent in the Southwest CRD. By May 13, 60 percent of corn had been planted in the West Southwest CRD, and 15 percent in the Southwest CRD.

During April and early May, streamflows at the Iroquois River and Silver Creek sites were near their long-term means, 1923-89 and 1970-89, respectively (fig. 2). Streamflow in the Sangamon River was slightly below the long-term mean, 1914-89. During the week of May 15-21, 5 to 6 in. (inches) of rain fell on the Silver Creek area, and 2 to 3 in. of rain fell on the other two watersheds. On May 17, Silver Creek near Freeburg had a peak discharge of 11,000 ft^3/s (cubic feet per second)--a new maximum discharge for the period of record. The recurrence interval for this discharge was 10 years. The magnitude of the flood events on the Sangamon River at Monticello and the Iroquois River at Chebanse were less; the recurrence intervals for these floods are 5 and less than 2 years, respectively (Curtis, 1987).

The storms of May 15-21 were considered to be critical runoff events. A critical runoff event, in terms of timing and intensity, occurs up to 2 weeks after pesticide application, has at least 0.4 in. of rain, and has a runoff volume that is 50 percent or more of the precipitation (Wauchope, 1978). During a critical event, up to 2 percent of the amount of herbicide applied could be lost to runoff. These losses could be much higher if the storm is the first significant precipitation to fall on the site after application of the herbicides. Wauchope (1978) also noted that a small rain, soon after herbicide application, can produce large concentrations of herbicides in the runoff as a result of low runoff volume and high pesticide residues in the field.

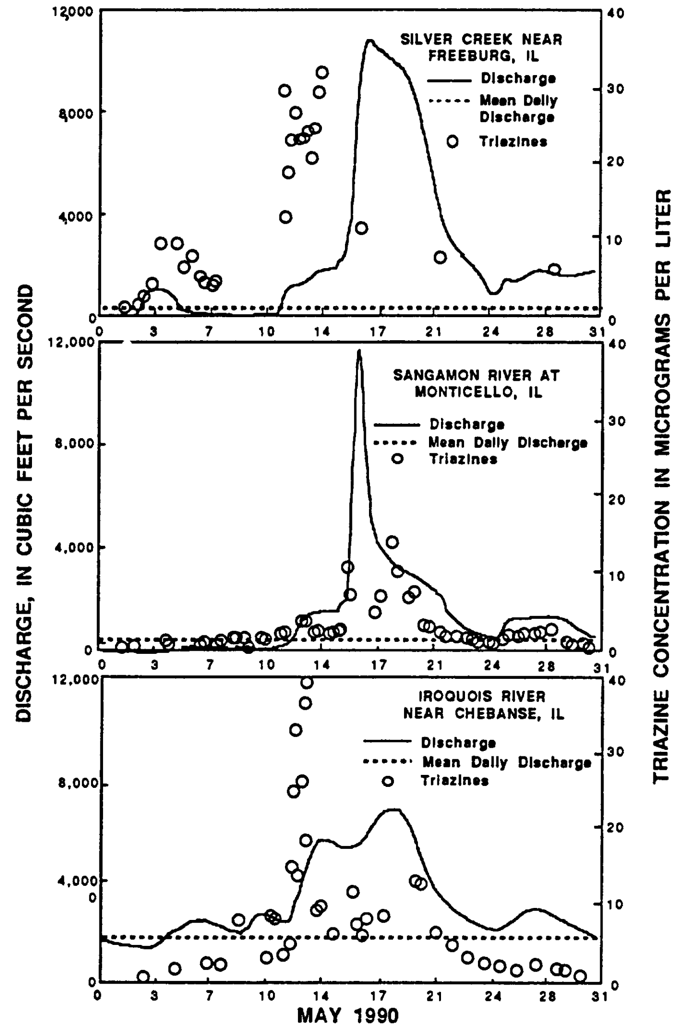

Figure 2. Discharge hydrographs and triazine concentrations, May 1990.

RESULTS AND DISCUSSION

On May 12, 5 days of steady rain began in the study area and culminated in heavy thunderstorms on May 16 and 17 in all three drainage basins. On May 12, at 1100 hours, the concentration of triazine herbicides at the Silver Creek site was 30 μg/L (fig 2.). Following this initial peak, the concentrations declined to 13 μg/L at 1300 hours. Samples that were collected every 6 hours for the next 2 days had concentrations of triazines of approximately 22 μg/L. Triazines reached a peak of 32 μg/L on May 14 at 1745 hours. On May 14, the automatic sampler was flooded, and the next sample was not collected until May 17 at 1330 hours, near the peak discharge. At this time, the concentration was 12 μg/L, but, because of the large volume of water present in the creek, the herbicide load was large. Samples were collected manually for the rest of May. The triazine concentrations decreased quickly.

Discharge in the Sangamon River at Monticello steadily declined until the morning of May 12, when the same storm system that affected Silver Creek appeared (fig 2.). Prior to May 12, the concentrations of triazines ranged from 0.2 to 2 µg/L. The concentration of triazines increased steadily with increasing discharge until the peak concentration, 11 µg/L, was reached at about 1300 hours on May 16. The peak triazine concentration occurred several hours before the peak discharge of 11,000 ft^3/s at 1800 hours. The automatic sampler ceased functioning at this time, and no more samples were collected until the morning of May 18. On May 18 at 0800 hours, the concentration of triazines was 4.9 µg/L; then the concentration increased steadily with no corresponding increase in discharge, to a peak of 14 µg/L on May 19 at 0800 hours. Concentrations of triazines then declined for the rest of May, returning to their prestorm concentrations.

Concentrations of triazine herbicides at Iroquois River near Chebanse at the beginning of the month of May were 0.4 µg/L (fig. 2). By 1700 hours on May 12, several small storms had moved through the basin, and the concentration of triazine herbicides was 2.0 µg/L. The discharge then began to increase as a result of the same storm described at the other two sites. The concentration of triazines increased to a peak of 37 µg/L on May 13, well before the peak discharge of 6,010 ft^3/s on May 15. The discharge had declined slightly when another storm caused an increase in the discharge to 7,380 ft^3/s on May 19. The concentrations of triazines peaked at 13 µg/L on May 20, 24 hours after the discharge peak. This peak concentration was less than half that recorded on May 13. Triazine concentrations and discharge declined during the rest of May.

SUMMARY

In the spring of 1990, the USGS in Illinois installed automatic samplers for the collection of surface-water samples at three sites in Illinois. The samples were used to quantify the magnitude and duration of the concentration of triazine herbicides during the critical time following the application of herbicides.

A major storm in mid-May 1990 affected all three sites. Silver Creek near Freeburg had a record peak discharge of 11,000 ft^3/s on May 17. The recurrence interval for this flood was 10 years. The recurrence interval for the flood on May 16 at the Sangamon River at Monticello and the Iroquois River near Chebanse on May 15 was 5 and less than 2 years, respectively.

In the Silver Creek basin, triazine concentrations increased sharply during even small storms. A peak of 32 µg/L was observed several days before the peak discharge. A different pattern was demonstrated at the Sangamon River at Monticello. Concentrations of triazines did not change rapidly and did not reach the levels measured in Silver Creek. The peak concentration of 14 µg/L occurred several days after the peak discharge. The Iroquois River near Chebanse had a peak triazine concentration of 36 µg/L on May 13, 2 days before the peak discharge. On May 19, another storm produced a peak discharge of 7,380 ft^3/s. The peak triazine concentration associated with this event reached 13 µg/L on the following day.

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DISTRIBUTION OF SELECTED ANTHROPOGENIC ORGANIC COMPOUNDS ON SUSPENDED SEDIMENT IN THE MISSISSIPPI RIVER

By Colleen E. Rostad[1] and Wilfred E. Pereira[2]

ABSTRACT

Transport of organic contaminants on suspended sediment in the Mississippi River was investigated as part of an ongoing, multidisciplinary study. Suspended sediments from 17 sites along the lower and middle Mississippi River and its major tributaries were sampled 4 times during 1988 through 1990 at different seasons and riverflow conditions. Large-volume (500 liter) water samples collected at each cross section were weighted for water discharge to reflect the riverflow accurately at each vertical. Suspended sediments were isolated from the riverwater samples by continuous- flow, high-speed centrifugation. The samples were then air-dried, extracted, and analyzed for selected halogenated organic compounds, including chlordane, nonachlor, chlorothalonil, dachthal, hexachlorobenzene, pentachloroanisole, and polychlorinated biphenyls. The concentration on the suspended sediment was converted to nanograms per gram organic carbon. Seasonal fluctuations in river discharge affected the distribution and transport of these compounds in the suspended sediment of the Mississippi River.

INTRODUCTION

The Mississippi River basin drains 41 percent, or 2.97 million square kilometers of the contiguous United States. Many water-quality studies, including studies of water, bed sediment, and biota, have been done to assess the effects of pollutants on this large river system. There are few published studies regarding the transport of organic compounds on suspended sediment. The Ohio River contributes about 50 percent of the water but only about 37 percent of the sediment in the Mississippi River. In contrast, about 15 percent of the water and at least 40 percent of the sediment in the Mississippi River is contributed by the Missouri River. With such distinctive differences in input from these two major tributaries, it is conceivable that the distribution of organic compounds on the suspended sediment may be affected. Consequently, an assessment of the occurrence and distribution of organic contaminants is needed to provide a basis for evaluating pollutant transport on the suspended sediment. This paper describes seasonal variations in factors involved in the transport of selected anthropogenic compounds on the suspended sediment in the Mississippi River. Sampling locations included sites on the Illinois, Mississippi, Missouri, Ohio, White, Arkansas, and Yazoo Rivers, and on the main stem of the Mississippi River at St. Louis, Mo., Thebes, Ill,, Hickman, Ky., Fulton, Tenn., Helena, Ark., Arkansas City, Ark., Vicksburg, Miss., Old River Outflow Channel, La., St. Francisville, La., and Belle Chasse, La.

METHODS

Representative discharge-weighted suspended-sediment samples were collected in May-June 1988, March-April 1989, June 1989, and February-March 1990 at 17 sites along the lower Mississippi River and its major tributaries, using techniques previously described by Nordin and others (1983) and Meade (1985). From upstream to downstream, the sample sites were Illinois River at Meredosia, Ill., Mississippi River near Winfield, Mo., Missouri River at Hermann, Mo., Mississippi River at St. Louis, Mo., Mississippi River at Thebes, Ill., Ohio River at Olmsted, Ill., Mississippi River below Hickman, Ky., Mississippi River at Fulton, Tenn., Mississippi River at Helena, Ark., White River at Mile 11.5, Ark., Arkansas River at Pendleton, Ark., Mississippi River above Arkansas City, Ark., Yazoo River at Mile 9.0, Miss., Mississippi River below Vicksburg, Miss., Old River Outflow Channel near Knox Landing, La., Mississippi River near St. Francisville, La., and Mississippi River below Belle Chasse, La. Lagrangian sampling strategy was used; this strategy involves following a parcel of water as it moves down the river channel, as determined from average mean velocity. The large-scale discharge-weighted water sample was pumped at each vertical either from one-half depth, or at a maximum depth of 5 meters. The water was pumped through Teflon[3] tubing by a Teflon, air-driven, double-diaphragm pump, into a continuous-flow, high- speed centrifuge operating at 16,000 revolutions per minute. Sediment particles smaller than 63 μm (micrometer) with a nominal size of 370 nanometers were removed according to Rees and others (1991). All exposed centrifuge surfaces were coated with or directly machined from Teflon to minimize sample contamination and site-to-site carryover. The suspended sediment was deposited in a centrifuge bowl which was lined with a removable Teflon sheet. This Teflon liner was transferred to a Teflon bag, where the suspended-sediment sample was gently resuspended. The sample was air-dried, ground, weighed, and spiked with a synthetically labeled surrogate compound (decafluorobiphenyl) to verify extraction efficiency. The sediment sample was extracted with an ultrasonic probe, thrice with acetone and once with hexane. The extracts were combined, concentrated, and spiked with internal standards prior to analysis by gas chromatography/negative ion chemical ionization/mass spectrometry. This technique is more sensitive and more selective than the more conventional electron impact mass spectrometry (Ribick and others, 1982).

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[3] The use of trade names in this paper is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

RESULTS

The discharge in the Mississippi River steadily increased upstream to downstream during each sampling trip. Higher discharge occurred during spring runoff on the Ohio River in March 1989 and March 1990. Although the discharge in the river steadily increased from upstream to downstream, the suspended-sediment concentration did not. The suspended sediment concentration finer than 63 µm ranged from 100 to 200 milligrams per liter, except during May-June 1988, when the suspended-sediment concentration was significantly lower at each site because of low-flow conditions. The percent organic carbon on the suspended sediment was consistent at all sites from each trip--about 2 percent; however, the percent organic carbon was higher during the drought conditions in May-June 1988, when it averaged about 3.5 percent.

Pentachlorophenol is a widely used general herbicide, wood preservative, and insecticide for termite control. It was analyzed for but not detected. However, pentachloroanisole, a degradation product of pentachlorophenol, was detected. Concentrations of pentachloroanisole were two to four times higher during spring runoff in March 1989 and 1990 than in May-June of 1988 and 1989. Concentrations of up to 110 ng/gOC (nanograms per gram organic carbon) on the suspended sediment were seasonally related to spring runoff. It is likely that pentachlorophenol is present in the bed sediments of the Mississippi River, where it is converted to pentachloroanisole. During periods of high flow, resuspension of this material results in increased concentrations of pentachloroanisole on the suspended sediment. This observation is in contrast to the distribution of chlordane, which was found in higher concentrations (up to 250 ng/gOC) on the suspended sediment during periods of low discharge, especially during the drought in May-June 1988, than during spring runoff in March of 1989 and 1990 when concentrations averaged about 75 ng/gOC. The source of the chlordane on the suspended sediment is not from resuspension of chlordane-contaminated bed sediment. Chlordane is toxic to humans; its use was restricted by the U.S. Environmental Protection Agency in 1979, and banned in 1985 except for residential termite control.

Dachthal is a preemergent herbicide and was quite common in these samples. High concentrations of up to 35 ng/gOC were observed during May-June 1988 at the upper river sites, above the Ohio River confluence. During March-April 1989, there was an unexplained sharp increase in the concentration to 50 ng/gOC in the White River, possibly because of an isolated spill or runoff event that did not occur in previous or subsequent trips. Otherwise, no distinct seasonal or spatial trends in dachthal distributions were seen.

The total polychlorinated biphenyls (PCB) reported here were determined by summing the total penta-, hexa-, hepta-, and octachlorobiphenyls. Considering their extensive industrial use in the past, it is not surprising that PCB were detected in every sample of suspended sediment. Relatively low concentrations were seen in suspended sediment in the Missouri River, and higher concentrations in suspended sediment in the Illinois River. The suspended sediment in the Ohio River contained very high concentrations (up to 7,500 ng/gOC), which prevailed throughout the remainder of the river. This upriver-to-downriver trend was similar for each sampling trip, although slightly higher concentrations of total PCB were observed during spring runoff. It is likely that the high concentrations of total PCB on the suspended sediment derive from erosion of surface sediment or resuspension of bed material that contains elevated concentrations of these persistent materials.

SUMMARY

Concentrations of organic contaminants on suspended sediment in the Mississippi River were determined from 17 sites along the lower and middle Mississippi River, and its major tributaries during 1988 through 1990. Seasonal fluctuations in river discharge affected the distribution and transport of these compounds in the suspended sediment of the Mississippi River. Concentrations of pentachloroanisole and PCB increased during periods of spring runoff, when resuspension of bottom sediment likely occurs. Chlordane concentrations were higher during low-flow periods.

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PLANS FOR RESEARCH OF NONPOINT-SOURCE GROUND-WATER CONTAMINATION IN THE COASTAL PLAIN OF THE NORTHEASTERN UNITED STATES

By Anthony S. Navoy[1], Eric F. Vowinkel[1], Herbert T. Buxton[1] *and* Paul E. Stackelberg[2]

ABSTRACT

Nonpoint-source ground-water contamination results from the introduction into the recharge process of compounds whose use, existence, or application can be ubiquitous and therefore can affect a wide area. Additionally, the aggregation of many local, individual point sources of contaminants can result in broad areas of contamination. In each of these cases, the definition and management of the source(s) and prediction of the consequences can be difficult without an understanding of the hydrologic processes that affect the movement of contaminants once introduced into ground water.

An investigation is proposed that will examine nonpoint-source ground-water contamination processes under current conditions in Long Island, New York, and southern New Jersey. The objectives of this investigation are to (1) describe the effects of human activities on regional ground-water quality; (2) investigate the processes affecting the source, integration, and transport of nonpoint-source contaminants in the ground-water system; and (3) develop methods for quantifying and analyzing nonpoint-source ground-water contamination at the local and regional scale.

INTRODUCTION

The introduction of contaminants into ground-water systems through natural and artificial recharge processes or by direct injection can degrade the quality of ground-water supplies and, in some areas, can pose a significant public-health threat. The contamination is derived from a variety of sources that can be related to human activities. These sources have been categorized by some investigators as point or nonpoint on the basis of the observer's understanding of the circumstances surrounding the actual introduction of contaminants into ground water and on the areal extent (scale) of the resulting contamination. Although this categorization can be considered relative and nonexclusive, this investigation focuses on contaminants that are present over a wide area and that, for practical purposes, can be considered nonpoint-source contaminants.

Compounds that are introduced into the recharge process and whose existence, use, or application can lead to contamination over a broad area include fertilizers, pesticides, and defoliants used, for example, in agriculture, along roadsides, and(or) in parks or golf courses. The aggregate effect of many local, individual point sources of contaminants also can result in a broad area of contamination. Examples of nonpoint-source contamination from a regional perspective include the use of the aforementioned chemicals on residential lawns and commercial landscapes as well as discharge of effluent from septic tanks, leakage from underground storage facilities, infiltration of urban or highway runoff, and improper disposal or handling of products, cleaners, solvents, and greases in commercial, residential, and industrial areas. Understanding and quantifying the process of nonpoint-source contamination requires an integration of information about multiple and diverse contaminants, sources, and mechanisms with knowledge of the hydrogeologic and geochemical processes that affect contaminant transport at local and regional scales. This understanding is essential in any attempt to limit the deleterious effects of human-induced contaminants and to manage water resources effectively.

An investigation is proposed that will examine nonpoint-source ground-water contamination processes. This paper outlines the general direction of research for this investigation.

PLANS FOR RESEARCH

Objectives

The proposed investigation will examine nonpoint-source ground-water contamination processes. The objectives of this investigation are to (1) describe the effects of human activities on regional ground-water quality; (2) investigate the processes affecting the source, integration, and transport of nonpoint-source contaminants in the ground-water system; and (3) develop methods for quantifying and analyzing nonpoint-source ground-water contamination at the local and regional scale.

Study Area

The northeastern U.S. Coastal Plain presents an opportune location to study nonpoint-source ground-water contamination processes. The investigation will focus on the Coastal Plain of Long Island, N.Y., and of southern New Jersey (fig. 1). This area is typical of large population centers that derive their water supply from regional ground-water systems. A diversity of land use consisting of industrial, commercial, residential, and agricultural sites has introduced a broad spectrum of contamination into the ground-water system for a long period. In addition, the Coastal Plain hydrogeology has been defined by previous investigators, and a large ground-water-quality data base is available. The results of this investigation could be useful in other areas with similar land use and hydrogeology.

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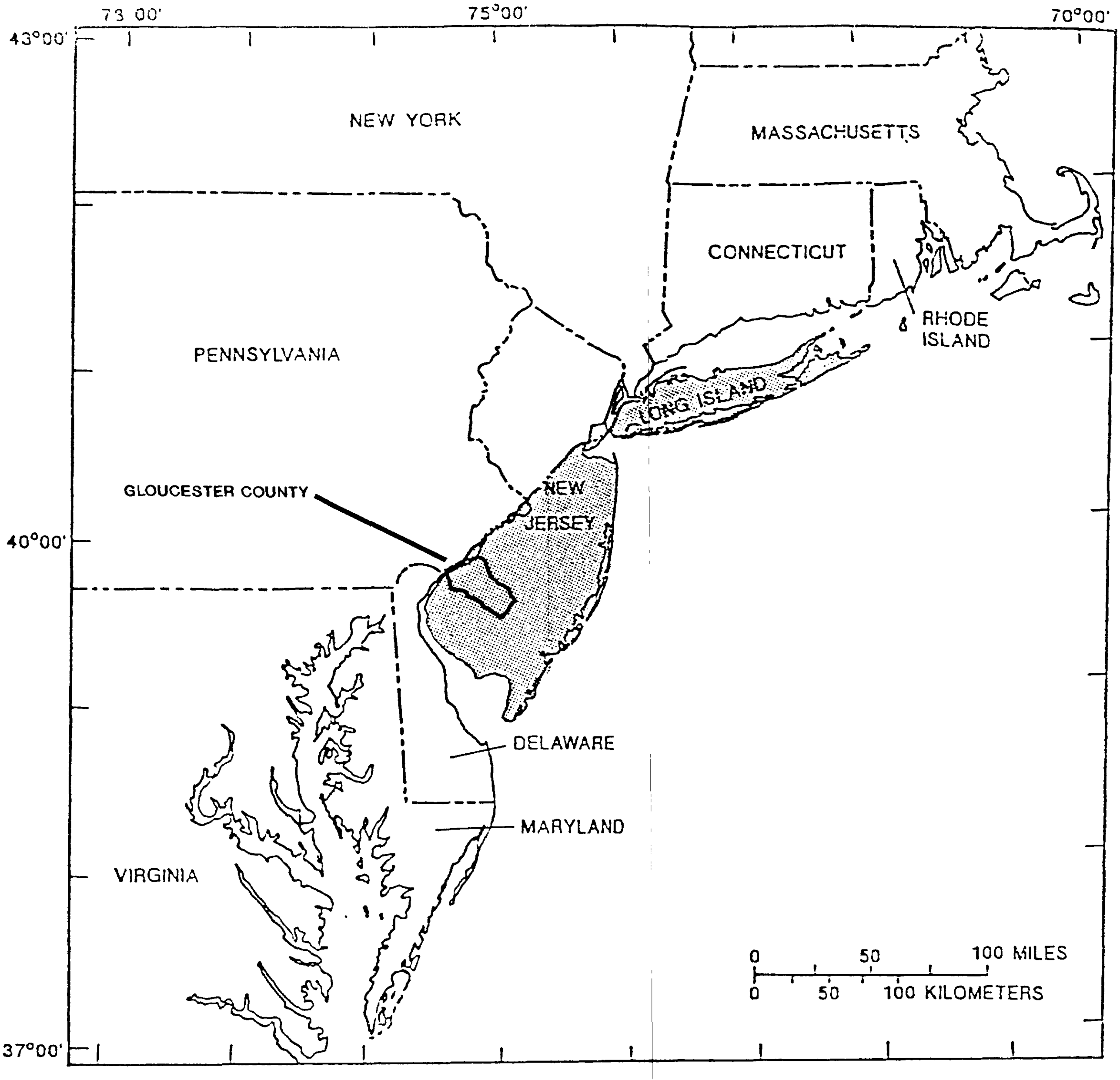
73°00'
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NEW YORK
MASSACHUSETTS
CONNECTICUT
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PENNSYLVANIA
LONG ISLAND
GLOUCESTER COUNTY
NEW JERSEY
DELAWARE
MARYLAND
VIRGINIA
0 50 100 MILES
0 50 100 KILOMETERS

Figure 1. Location of the study area in the Coastal Plain of New York and New Jersey.

Approach

The investigation will have a two-part focus: to characterize the effects of human activities on shallow, regional ground-water quality, and to develop an understanding of the processes that govern the transport of "nonpoint-source type" contaminants within a regional ground-water system. On the basis of the methods used and study results of these two investigation components, a general methodology will be described that could be applied to other areas. Several study areas within the Coastal Plain of Long Island, N.Y., and of southern New Jersey, will be investigated in detail. The selection of study areas will depend on the availability of high-resolution land-use data, ground-water-quality data, and hydrogeologic information from local, State, and Federal sources, including the U.S. Geological Survey.

Characterization of the Effects of Human Activities on Shallow Ground-Water Quality

As part of the first component of this investigation, an analysis will be conducted to determine the relations between human activities (as represented by land use and other surrogate variables) and shallow ground-water quality to quantify the type, distribution, and amount of contaminants from the land surface that enter the ground-water system. Contaminant-source distribution and loading are important factors in the evaluation of changes in shallow ground-water quality throughout a region in that they provide the data needed to identify high-risk human activities and the input to regional ground-water transport models.

Previous investigators (Eckhardt and others, 1989; Vowinkel and Battaglin, 1989) have studied the relations between land use and shallow regional ground-water quality and have explored the use of various statistical models to quantify these relations. These models, developed either for Long Island or for New Jersey, will be applied to the selected study areas in order to determine source distribution and loading, and to define the spectrum of contaminant compounds that characterize individual land-use patterns. These statistical models will be improved by using higher resolution information on the distribution of human activities and more detailed hydrogeologic data. Two sources of this type of data that can be used to accomplish this goal in the study area are available: (1) digitized land-use data at a scale of 1:24,000 for a large area of Long Island, N.Y.; and (2) land-use data at a scale of 1:4,800 for Gloucester County, N.J., compiled at 5-year intervals from about 1970 to present (1990). The finer scale land-use data will permit the resolution of important but small source areas that would otherwise be located improperly or overlooked. The temporally oriented land-use data will permit analyses relating water quality at a specific depth (or age) in the ground-water system to the land use at the time of entry into the system.

The use of additional or alternate surrogate variables to represent various human activities and their potential for nonpoint-source contamination will be explored. The most promising of the surrogate variables is the new Standard Industrial Use Code which will permit the definition of industry types (for example plastics, petroleum, and so forth) to be related to the distribution and type of source contaminants. The most important hydrogeologic variables that could be introduced into these statistical models relate to unsaturated-zone properties that control a constituent's passage to the water table. An areally extensive data set of these properties may, however, be difficult to obtain.

Investigation of Nonpoint-Source-Contaminant Fate and Transport

The second component of this investigation addresses the transport of nonpoint-source contaminants after they enter the subsurface. The investigation of the transport of nonpoint-source contamination requires an understanding of the hydrologic factors that determine the ground-water flow field at a regional scale. The pattern of advective contaminant transport can be used as a baseline from which to evaluate the effects of chemical and biological processes on the dispersal of a contaminant within the ground-water system. The relations between land use and shallow ground-water quality developed as part of the first component of this investigation will provide the source term (input) to regional transport analysis. These relations also will provide a means to identify the most significant contaminants on the basis of their significance to public health and their mobility in the ground-water system.

The advective transport of contaminants after entry into the ground-water system is assumed to be controlled mainly by hydrogeologic factors. The development of ground-water models that include these factors provides the ability to understand and analyze contaminant flow paths at regional scales. Within the study area, several models of differing scale will be used to aid in the analysis of nonpoint-source contamination. These are the Long Island regional model (Buxton and others, 1991); a finely gridded cross-sectional model through Long Island (Buxton and Modica, 1989); and a local-scale flow model of Greenwich Township, Gloucester County, N.J. (A.A. Pucci, Jr., and Cynthia Barton, U.S. Geological Survey, oral commun., 1990), a highly industrialized (and highly contaminated) area of the New Jersey Coastal Plain with multiple documented point sources.

These ground-water-flow models have a particle-tracking capability that will be used to establish the relation of contaminant concentration to distance along a flow path. The movement of contaminants along specific flow paths and the consistency of contaminant presence relative to source- area land use and land-use change will be evaluated using the model. A three-dimensional representation of contamination within a regional aquifer will be attempted. This representation will be based on temporally varying land-use data, associated contaminant source terms inferred from relations of land use to water quality, and flow-model-derived time-of-travel contaminant positions. The analysis will be refined in an attempt to incorporate the statistically derived contaminant source terms into ground-water solute-transport models for a comparison of theoretical concentrations to observed contaminant-concentration data. Differences between simulated and observed water quality will be evaluated and related to appropriate transport or geochemical processes.

CONCLUSIONS

The results of this investigation are expected to provide insight into the processes that control the introduction and transport of nonpoint-source contaminants into the ground-water system. The methodology developed to identify significant contaminants, estimate loadings and distributions, and evaluate transport in local and regional ground-water flow systems will help develop strategies for monitoring and controlling nonpoint-source contamination.

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PRELIMINARY ANALYSIS OF WATER-QUALITY DATA FROM THE SHALLOW, INTERMEDIATE, AND DEEP ZONES OF FIVE LAND-USE AREAS ON LONG ISLAND, NEW YORK

By Paul E. Stackelberg[1] and Edward T. Oaksford[1]

ABSTRACT

Water-quality data obtained from three depth intervals in five areas of differing land use on Long Island, N.Y., were compared to determine whether effects of land use that are observed in the shallow zone can be recognized in deeper parts of the aquifer. The water-quality data consisted of chloride, potassium, nitrate, and dissolved solids concentrations. The five study areas represent differing degrees of development and are categorized as (1) long-term sewered suburban, (2) recently sewered suburban, (3) unsewered suburban, (4) agricultural, and (5) undeveloped. These study areas lie along the regional ground-water divide, where the predominant direction of ground-water flow is vertically downward.

Median concentrations of the four constituents in the shallow and intermediate depth zones were highest within the agricultural or long-term sewered suburban areas and lowest within the undeveloped area. Median concentrations in the deep zone were typically highest within the long-term sewered suburban area and lowest within the unsewered suburban area. Time-of-travel data indicate that the elevated median concentrations within the deep zone are probably the result of pumping, which accelerates the downward movement of water and its chemical constituents. Comparison of the deep-zone and shallow-zone data among the three suburban areas suggests that the elevated nitrate concentrations in the deep zone of the long-term sewered suburban area reflect historical nitrate-loading patterns, and the elevated nitrate concentrations in the shallow zone of the unsewered suburban area reflect current nitrate-loading patterns.

Results indicate that, in areas where the predominant flow direction is vertical, water-quality patterns observed in shallow parts of the aquifer system tend to be reflected at depth.

INTRODUCTION

This study was designed as a preliminary evaluation of water-quality data from three depth intervals beneath five different land-use areas on Long Island, N.Y. (fig. 1). The data were statistically analyzed to determine whether effects of development that are observed in the shallow zone are evident in deeper parts of the aquifer. Because this was a preliminary study, only four water-quality constituents were evaluated--chloride, potassium, nitrate, and dissolved solids.

The effect of land use on ground-water quality is of great concern on Long Island, which is heavily populated and developed, and relies on ground water as its sole source of potable water. Previous investigations by Eckhardt and others (1989) and S.J. Cauller and others (U.S. Geological Survey, written commmun., 1990) examined the effects of human activities on the shallowest part of the ground-water system on Long Island. Whether these effects are evident along projected flow lines in deeper parts of the aquifer system has not been determined, however.

Water-quality data were obtained from five areas of differing land use on Long Island that represent a complete range of development. The five study areas lie along the regional ground-water divide (fig. 1), where the predominant direction of ground-water flow is vertically downward. The five areas (fig. 1) are categorized as (1) long-term sewered (greater than 22 years) suburban, (2) recently sewered (less than 8 years) suburban, (3) unsewered suburban, (4) agricultural, and (5) undeveloped. Conservative contaminants introduced at the water table in areas of vertical recharge will move downward into the aquifer system at rates proportional to local vertical hydraulic conductivities and gradients. A preliminary evaluation of vertical flow rates was coupled with statistical analysis of water-quality data to determine the extent of movement of chemical contaminants from shallow to deeper parts of the aquifer system.

This paper describes the preliminary evaluation of four water-quality constituents from three depth intervals in the Long Island aquifer system. Results obtained for intermediate-depth and deep zones are compared to shallow water-quality data to determine whether effects of land use observed in the shallow zone can be recognized in deeper parts of the aquifer system.

DATA COLLECTION

The data consisted of analyses of samples from 88 shallow wells, 70 intermediate-depth wells, and 52 deep wells within the five study areas. The shallow zone was represented by 15 to 20 wells in each study area, the intermediate zone by 10 to 23 wells, and the deep zone by 13 to 23 wells. The agricultural and undeveloped areas had no deep wells; the deepest wells available in these areas are screened in the intermediate zone, and times of travel to the screen midpoints are nearly equal to those at the intermediate-depth wells in the three suburban areas.

All wells screened in the shallow zone were monitoring wells; at each of these, a minimum of three casing volumes were evacuated, and drawdown, specific conductance, pH, and temperature were allowed to stabilize before sampling (Eckhardt and others, 1989). Wells screened in the intermediate and deep zones were predominantly industrial, public-supply, and irrigation wells; at each of these, a minimum of three casing volumes of water were evacuated, and measurements of specific conductance, pH, and temperature were made before sampling.

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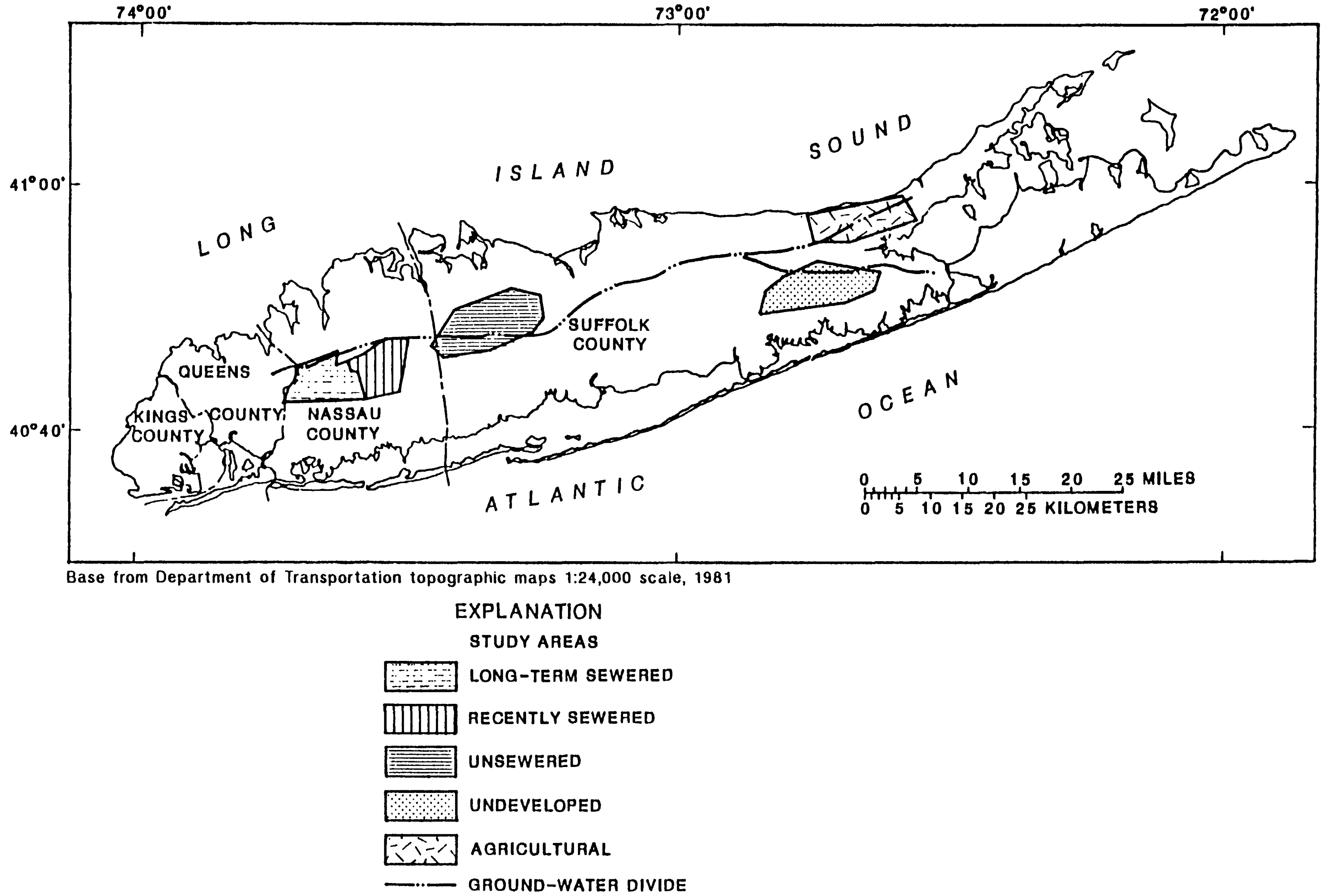
[1] U.S. Geological Survey, Syosset, N.Y.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LONG ISLAND SOUND
QUEENS COUNTY
KINGS COUNTY
NASSAU COUNTY
SUFFOLK COUNTY
ATLANTIC OCEAN
0 5 10 15 20 25 MILES
0 5 10 15 20 25 KILOMETERS
EXPLANATION
STUDY AREAS
LONG-TERM SEWERED
RECENTLY SEWERED
UNSEWERED
UNDEVELOPED
AGRICULTURAL
GROUND-WATER DIVIDE

Base from Department of Transportation topographic maps 1:24,000 scale, 1981

Figure 1. Location of the five land-use areas on Long Island, New York. (From Eckhardt and others, 1989, p. 398.)

METHODS

Wells were classified as shallow, intermediate-depth, or deep, according to the screen depth below the water table and the vertical flow rates within each study area (D.A. Eckhardt, U.S. Geological Survey, oral commun., 1990).

Estimates of vertical flow rates were calculated from cell-to-cell flow rates indicated by the regional ground-water flow model of Long Island (H.T. Buxton and D.A. Smolensky, U.S. Geological Survey, written commun., 1990). The model simulates ground-water flow under steady-state conditions for the period 1968-75. These years represent a period of record 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). Vertical flow rates were then used to calculate traveltimes along vertical flow paths to each screen's midpoint. Four wells that were indicated by modeling results to be in discharge areas were eliminated from analysis; these wells are near surface-water bodies where recharge enters a ground-water subsystem and subsequently discharges to its respective surface-water body.

Summary statistics calculated for water-quality data which contained censored values were performed through a log-probability regression technique (Helsel and Cohn, 1988), a robust procedure that minimizes rates of root mean square error. Censored value refers to a sample concentration reported as "less than the analytical detection limit."

The Kruskall-Wallis test was used to test the null hypothesis that the mean rank of the constituent concentration values between each study area were equal and that the mean rank of the screen depths below the water table within each study area were equal for all depth intervals. This test performs a one-way analysis of variance on rank-transformed data and is robust in that it is not sensitive to outlying values or to the assumptions of equal variance or normality.

If the null hypothesis was rejected by the Kruskall-Wallis test, indicating that at least one mean rank concentration value differed, or that at least one mean rank screen depth below the water table value differed, Tukey's honest significant difference test was performed to determine which means differed. The alpha value, or level of significance, for all hypothesis testing was 0.05.

RESULTS

For the shallow, intermediate-depth, and deep zones, median screened intervals below the water table ranged from 14 to 24 ft (feet), 68 to 304 ft, and 349 to 569 ft, respectively. Tukey's honest significant difference test indicates that, within each study area, significant differences exist between the mean ranks of the screened interval depths of each depth zone.

Water-quality data for the shallow wells in the five study areas are given in Eckhardt and others (1989) and in S.J. Cauller and others (U.S. Geological Survey, written commun., 1990) and are summarized here. Estimates of ground-water traveltime for each study area in each depth zone are shown in boxplots in figure 2. Summary statistics and results of Tukey's honest significant difference test are presented in table 1 and are discussed in the following paragraphs.

Comparison of water-quality data among the five study areas reveals similarities between the shallow zone and the intermediate zone. Although estimated median traveltimes (fig. 2) indicate that the intermediate zone does not reflect the effects of current development conditions, the land-use categories still reflect the relative degree of historical development within each study area. The lowest median concentrations of all four constituents in both the shallow and intermediate zones were in samples from the undeveloped area, and the highest median concentrations of all constituents except chloride in both zones were in the agricultural area. The highest median concentration of chloride in both zones was in the long-term sewered area. Although the highest median concentration of nitrate in both zones were in the agricultural area, Tukey's test results indicate that the mean rank of the nitrate concentrations here do not differ significantly from those in both zones of the three suburban areas. Within the shallow zone, the highest median concentrations of chloride were in samples from the long-term sewered area, but Tukey's test results indicate that the mean rank of the chloride concentrations is not significantly different from those for the shallow zone of the three suburban areas or the agricultural area. Within the intermediate zone, the highest median chloride concentration was also in the long-term sewered area, but Tukey's test results indicate that the mean rank of the chloride concentrations was not significantly different from that for the agricultural area.

Because the agricultural and undeveloped areas have no wells classified as being in the deep zone, the following discussion refers only to the three suburban study areas. Estimated median traveltimes (fig. 2) indicate that water quality within the deep zone in these areas should represent predevelopment conditions on Long Island, but the concentrations of the four constituents evaluated were slightly elevated and were highest in the long-term sewered area, the area with the longest history of development. This is attributed to the effects of local pumping, which accelerates the vertical migration of constituents into deeper parts of the aquifer system and is not completely accounted for by the Long Island regional flow model as a result of its coarse grid.

Data from the three suburban areas reveal similarities among all three depth zones. In all zones, the unsewered area had the lowest median concentrations of chloride, potassium, and dissolved solids, and the long-term sewered area had the highest median concentrations of chloride. The highest median concentrations of potassium and dissolved solids were in the intermediate-depth and deep zones of the long-term sewered area and in the shallow zone of the recently sewered area. Within the shallow zone, the unsewered area had the highest median nitrate concentrations, and the long-term sewered area had the lowest; within the deep zone the reverse was true--the

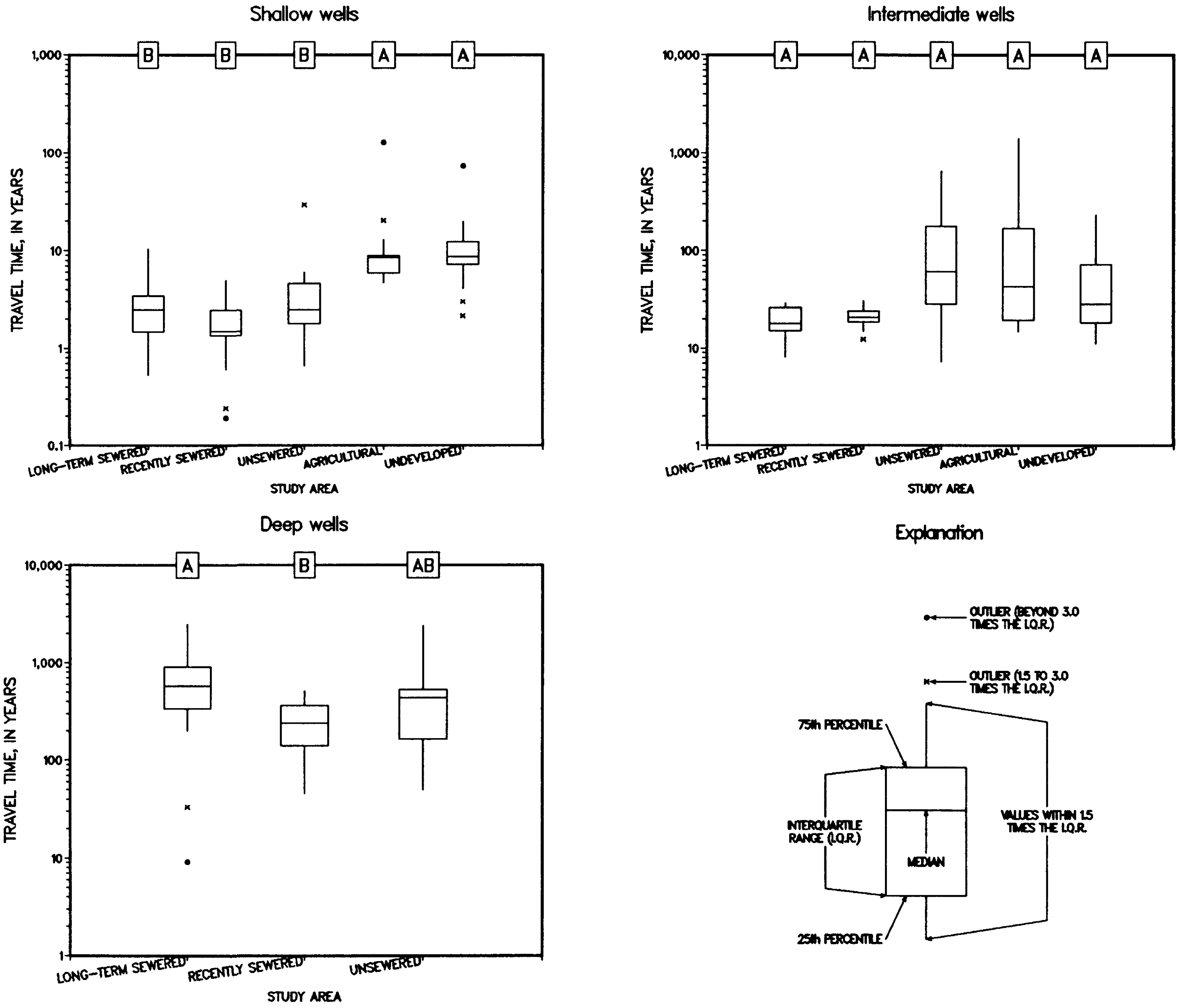

Figure 2. Estimated traveltime values within the shallow, intermediate, and deep zones of the five study areas. Letters above boxplots indicate results of Tukey's honest significant difference test. Groups of data with common letters do not differ significantly in traveltime.

Table 1. *Summary statistics and Tukey's test results for the five study areas*

[T, Tukey's honest significant difference test[1]; M, median concentration, in milligrams per liter; IQR, interquartile range of concentrations, in milligrams per liter]

Ground-water zone	Long-term sewered suburban			Recently sewered suburban			Unsewered suburban			Agricultural			Undeveloped		
	T	M	IQR	T	M	IQR	T	M	IQR	T	M	IQR	T	M	IQR
Chloride															
Shallow	A	31.6	21.2	A	30.8	36.2	AB	22.7	23.7	AB	23.4	13.6	B	8.30	14.4
Intermediate	A	42.9	31.6	B	14.9	23.5	B	7.10	12.1	AB	18.1	12.7	B	6.30	7.50
Deep	A	9.10	8.80	AB	6.05	9.55	B	3.40	3.10						
Potassium															
Shallow	AB	2.90	2.10	A	3.95	2.90	B	1.90	2.10	A	4.30	1.40	C	.800	.700
Intermediate	AB	2.00	1.10	BC	.900	1.50	BC	.800	.900	A	2.50	2.60	C	.400	.400
Deep	A	.900	.500	B	.550	.350	B	.500	.300						
Nitrate															
Shallow	AB	[2]5.05	[2]2.19	A	5.74	6.86	A	6.46	10.5	A	[2]8.91	[2]7.45	B	[2]240	[2]4.30
Intermediate	AB	[2]3.07	[2]3.35	A	4.25	5.30	AB	[2]1.17	[2]2.72	A	[2]4.37	[2]6.34	B	[2].009	[2]2.70
Deep	A	3.58	3.02	A	2.68	3.23	B	[2].500	[2].850						
Dissolved Solids															
Shallow	A	162	37.0	A	186	96.0	A	133	132	A	216	159	B	70.0	56.0
Intermediate	A	123	95.0	AB	84.0	114	B	49.0	79.0	A	144	97.0	B	41.5	56.0
Deep	A	79.0	68.0	AB	39.0	50.0	B	30.0	22.0						

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[1] Groups (study areas) of data with common letters do not have mean rank concentrations that differ significantly.

[2] Data contain censored values, statistics estimated through a log-probability technique (Helsel and Cohn, 1988).

unsewered area had the lowest median nitrate concentration, and the long-term sewered area the highest. This pattern probably reflects the influence of historical sewering practices. The highest median nitrate concentrations in the shallow zone, which contains relatively young ground water (fig. 2), are in the unsewered area as a result of continued nitrate loading from cesspool systems and lawn fertilizers. The highest median nitrate concentrations in the deep zone, which represents relatively old ground water (fig. 2), are in the long-term sewered area as a result of the longer period of loading of nitrates from cesspool systems, sewer-line exfiltration, and lawn fertilizers.

SUMMARY

Comparison of concentrations of four constiutents (chloride, potassium, nitrate, and dissolved solids) in ground-water samples from five areas of differing land use on Long Island, N.Y. reveal that the effects of development that are observed in shallow zones of the aquifer system are also evident in deeper zones. Samples from the shallow and intermediate zones of the undeveloped area had the lowest median concentrations of all four constituents, and samples from the same depth zones in the agricultural and long-term sewered area had the highest. Among the three suburban areas, the lowest median concentrations of chloride, potassium, and dissolved solids were in all zones of the unsewered area, and the highest median concentrations were generally in all zones of the long-term sewered area. These results indicate that, in areas where flow is predominantly downward, water-quality changes resulting from development that are evident within the shallow zones of the aquifer system are also reflected within the deeper zones.

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Helsel, D.R., and Cohn, T.A., 1988, Estimation of descriptive statistics for multiply-censored water-quality data: Water Resources Research, v. 24, no. 12, p. 1997-2004.

INVESTIGATION OF WATER QUALITY, BOTTOM SEDIMENT, AND BIOTA ASSOCIATED WITH IRRIGATION DRAINAGE FROM THE ANGOSTURA RECLAMATION UNIT AREA, SOUTHWESTERN SOUTH DAKOTA, 1988

By Earl A. Greene[1]

ABSTRACT

Water, bottom sediment, and biota were sampled during 1988 within the Angostura Reclamation Unit and adjacent areas in southwestern South Dakota. The study was conducted to determine the concentrations of major ions, selected trace elements, and pesticides in water, bottom sediment, and biota, and to compare the analytical results to various guidelines for environmental protection and to available baseline information.

Concentrations of trace elements in water delivered to Angostura Reservoir appeared to be similar to irrigation drainage water conveyed in return flow drains, and in the Cheyenne River downstream of the irrigated lands. In general, the study showed that toxicity from selenium or other trace elements and pesticides in water probably is not a persistent problem within the study area or downstream from irrigation return flows.

Trace-element concentrations in bottom sediment were similar to the geochemical baselines for soils of the Western United States. Pesticide concentrations in all samples of bottom sediment were less than laboratory analytical reporting limits.

With few exceptions, concentrations of elements and pesticides in biota generally were less than values known to produce harmful effects on growth or reproduction. Selenium concentrations in most whole-body fish tissue samples were greater than baseline values. Several other elements were present in biota at concentrations that were potentially elevated in comparison to baseline values, but concentrations of elements were not unusually high at any sites and no organisms were present in unusually large numbers.

INTRODUCTION

During the last several years, there has been increasing concern about the quality of irrigation drainage and its potentially harmful effects on human health, fish, and wildlife. Concentrations of selenium greater than water-quality criteria for the protection of aquatic life (U.S. Environmental Protection Agency, 1986a) have been detected in subsurface drainage from irrigated land in the western part of the San Joaquin Valley in California. In 1983, incidences of mortality, birth defects, and reproductive failures in waterfowl were discovered by the U.S. Fish and Wildlife Service at the Kesterson National Wildlife Refuge in the western San Joaquin Valley, where irrigation drainage was impounded. In addition, potentially toxic trace elements and pesticide residues have been detected in other areas in Western States that receive irrigation drainage. Because of these concerns, reconnaissance studies were conducted by scientists of the U.S. Geological Survey, U.S. Fish and Wildlife Service, and U.S. Bureau of Reclamation during 1986-89 to determine whether irrigation drainage from U.S. Department of Interior irrigation projects has caused, or has the potential to cause, significant harmful effects on human health, fish, and wildlife, or adverse effects on the suitability of water for other beneficial uses.

The Angostura Reclamation Unit in southwestern South Dakota (fig. 1) was chosen for study because most of the irrigated land and surrounding area overlie Cretaceous marine shales that are known to contain large concentrations of trace elements, including selenium. The Angostura Reclamation Unit is a flow-through system with one storage site, Angostura Reservoir, which is used to supply water for 12,200 acres of irrigated lands. The return flows from the irrigated lands do not discharge to a wildlife refuge and are not a direct source of drinking water. Irrigation return water drains to the Cheyenne River, which is a major drainage for western South Dakota as well as a major tributary to Oahe Reservoir and the Missouri River system.

This paper summarizes the results presented in a report by Greene and others (1990) that describes the results of a 2-year study to determine if potentially toxic constituents are present at concentrations sufficiently large to cause, or have the potential to cause, harmful effects on human health or on fish and wildlife within or immediately downstream from the Angostura Reclamation Unit. Concentrations of selected constituents were measured in water, bottom sediment, and biota; these concentrations were then compared to various standards, criteria, and to concentrations reported from other locations.

SAMPLE COLLECTION AND ANALYSIS

The objective of the sample collection and analysis was to determine if there are elevated concentrations of potentially toxic constituents associated with irrigation drainage. The constituents analyzed were major ions, trace elements, and pesticides. The pesticides analyzed in water, bottom sediment, and biota were selected based upon the common types of agricultural chemicals used on the irrigated lands.

The locations of sampling sites (fig. 2) were selected to identify any problem areas where constituent concentrations exceeded established standards and (or) criteria, or natural background (baseline) concentrations. In addition the sample locations were chosen to provide information on a diverse range of hydrologic, physical, and chemical conditions within the study area. Nine water and bottom sediment sampling sites were located throughout the study

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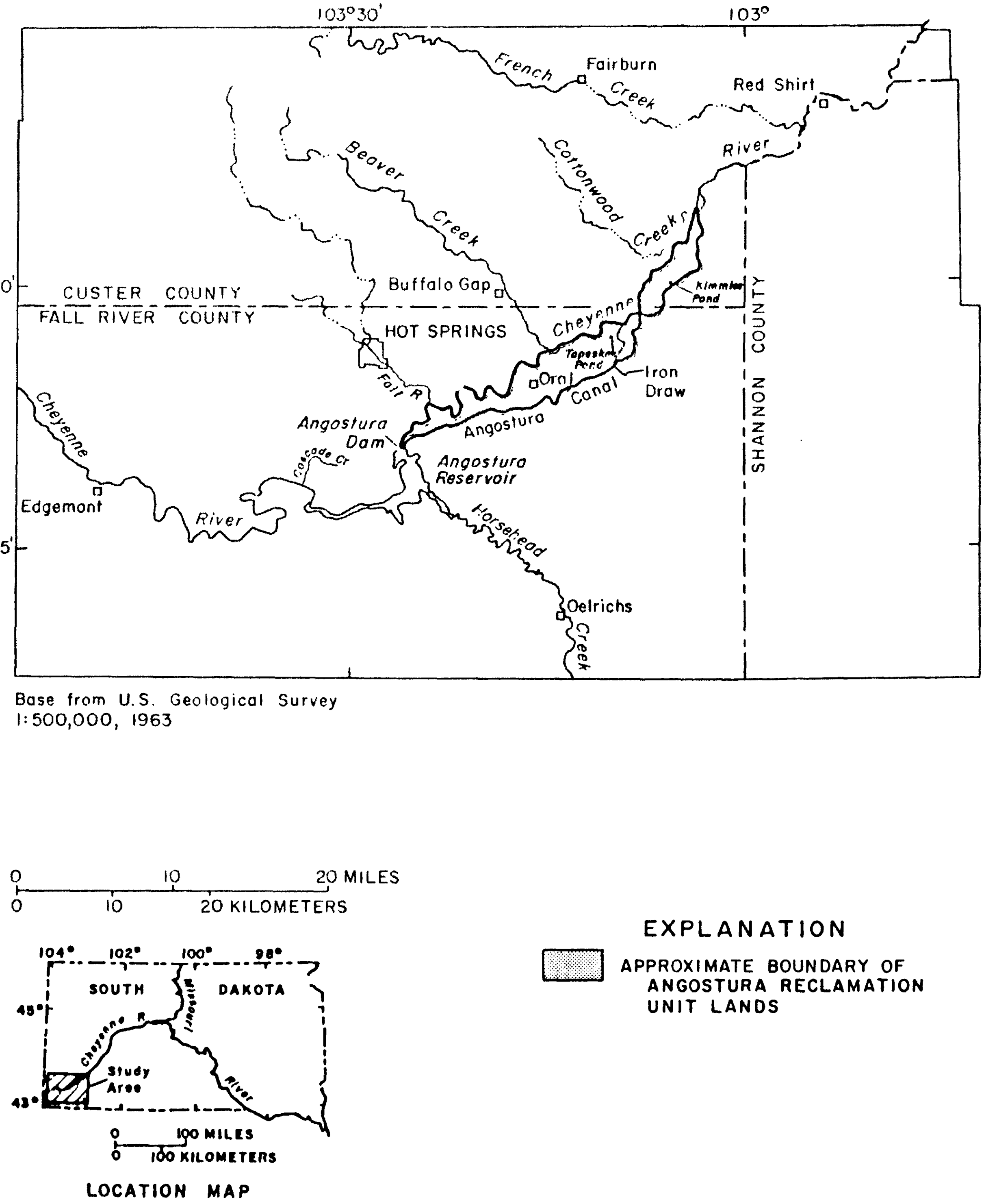
[1] U.S. Geological Survey, Rapid City, S. Dak.


103°30'
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French Creek
Fairburn
Red Shirt
River
Beaver Creek
Cottonwood Creek
Buffalo Gap
CUSTER COUNTY
FALL RIVER COUNTY
HOT SPRINGS
Cheyenne
Kimmie Pond
Topeska Pond
Oral
Iron Draw
Angostura Canal
Fall R
Angostura Dam
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Angostura Reservoir
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Edgemont
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Base from U.S. Geological Survey 1:500,000, 1963
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SOUTH DAKOTA
Cheyenne R
Missouri River
Study Area
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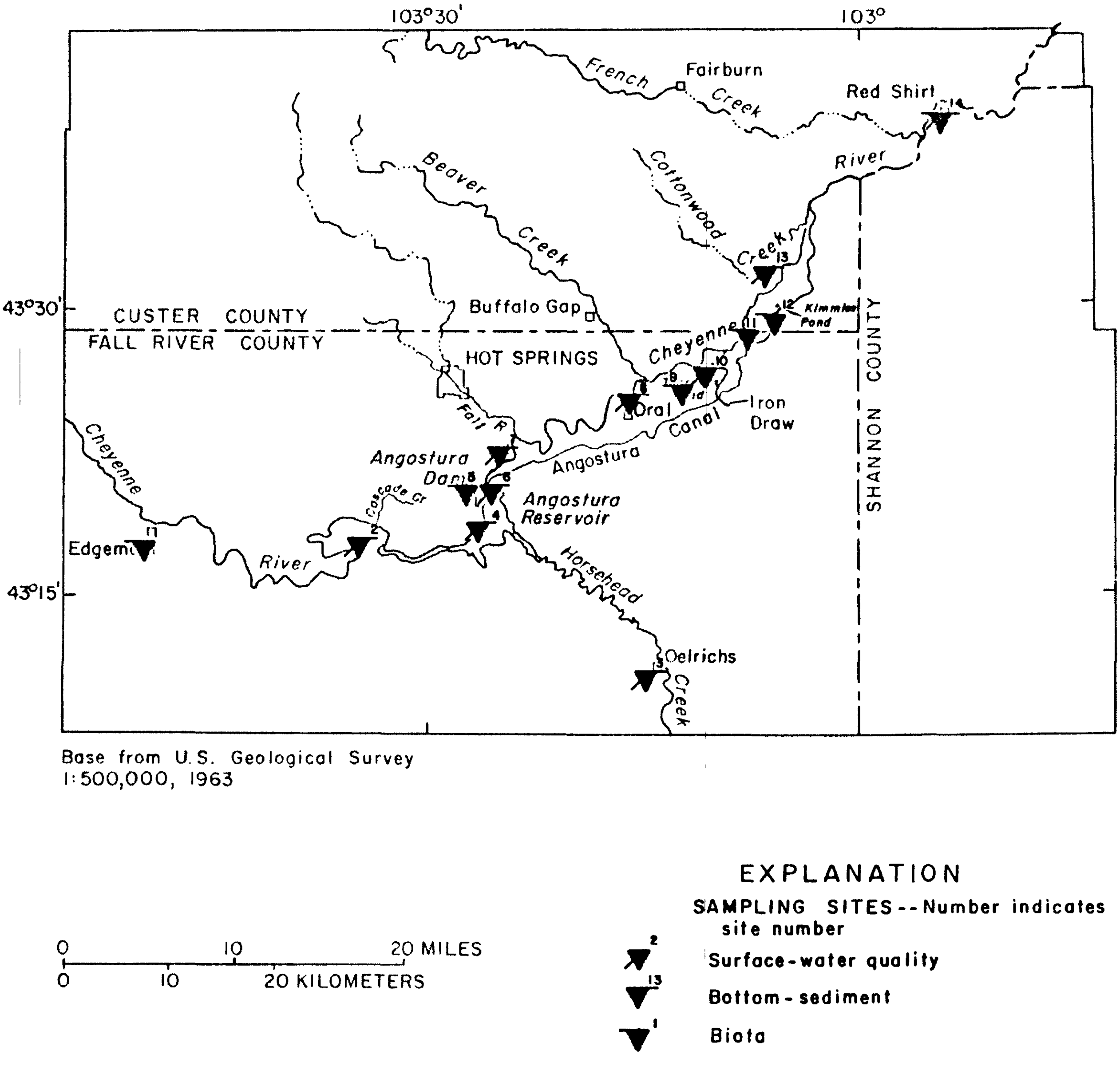
LOCATION MAP
EXPLANATION
APPROXIMATE BOUNDARY OF ANGOSTURA RECLAMATION UNIT LANDS

Figure 1. Location of study area.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FALL RIVER COUNTY
SHANNON COUNTY
12
Kimmins Pond
11
Cheyenne
10
9
HOT SPRINGS
Oral
Iron Draw
Canal
Angostura
Fall R
Angostura Dam
8
Cascade Cr
7
Angostura Reservoir
4
2
Cheyenne
River
Edgemont
1
Horsehead Creek
Oelrichs
3
Creek
0
10
20 MILES
0
10
20 KILOMETERS
EXPLANATION
SAMPLING SITES--Number indicates site number
2
Surface-water quality
13
Bottom-sediment
1
Biota

Base from U.S. Geological Survey 1:500,000, 1963

Figure 2. Location of sample sites.

area to characterize the chemical quality and bottom sediment chemistry of: the Cheyenne River upstream of irrigation, Angostura Reservoir, Angostura Canal, irrigation drains, and the Cheyenne River downstream of all irrigation return flow. Six biological sampling sites were located on or near the Cheyenne River to identify the presence of potentially elevated constituent concentrations in the biological community of the study area.

Water samples for chemical quality were collected according to techniques recommended by the U.S. Geological Survey (1977). Sample treatment and preservation were conducted by field personnel according to the requirements of the U.S. Geological Survey (1986). Analysis of major ions, trace elements, and pesticides were performed by the U.S. Geological Survey Water Quality Laboratory in Arvada, Colo., according to methods described in Fishman and Friedman (1985) for inorganic constituents, and Wershaw and others (1987) for pesticides.

Samples of bottom sediment were collected according to standards set for all irrigation drainage studies. Total concentration and organic content of trace elements were determined by a geochemistry laboratory of the U.S. Geological Survey in Lakewood, Colo. according to methods described in Severson and others (1987). Pesticide analyses of bottom sediment were conducted by the Hygienic Laboratory of the University of Iowa, Iowa City, Iowa, using standard U.S. Environmental Protection Agency (1986b) analytical methods.

Biota samples were collected using standard equipment and techniques (U.S. Fish and Wildlife Service, 1985a). All biota samples were analyzed by the University of Missouri Environmental Trace Substances Research Center and the Mississippi State Chemical Laboratory according to analytical methods approved by the U.S. Fish and Wildlife Service's Patuxent Analytical Control Facility in Laurel, Md. (U.S. Fish and Wildlife Service, 1985b).

RESULTS OF ANALYSES

Chemical quality of water from samples collected during 1988 throughout the study area is illustrated in figure 3. In general, the chemical quality of water flowing over alluvium and the Pierre Shale in the study area was a sodium sulfate type (sites 3, 6, 8, 10, 13, and 14). Exceptions were at site 2, where the water was a calcium sulfate type, and at site 7 where the water was a calcium bicarbonate type. The source of water at these two sites is spring flow, probably originating from Paleozoic limestones.

Average dissolved-solids concentration was the largest in the Cheyenne River upstream of irrigation (site 2) and the smallest in Fall River (site 7). Except for Fall River, which had an average dissolved-solids concentration of 952 mg/L (milligrams per liter), water in the study area generally had an average dissolved-solids concentration of greater than 1,000 mg/L (fig. 3).

The distribution of selected trace-element concentrations in water (fig. 4) show most were distributed near the analytical reporting limit, with the exception of molybdenum, selenium, uranium, and zinc. Uranium and zinc had the widest range of sample concentrations.

Overall, there appeared to be little difference among the concentration of trace elements in Cheyenne River water (site 2) upstream of Angostura Reservoir, irrigation drainage water conveyed in return flow drains (site 10), and Cheyenne River water downstream of the Angostura Reclamation Unit lands (site 14). This similarity may indicate that irrigation return water consists largely of excess surface runoff from irrigation and shallow ground-water return flow moving downgradient through the alluvium. Except for a few instances, trace-element concentrations measured at sites 2, 10, and 14 were similar. The median value of molybdenum (14 µg/L (micrograms per liter)) was slightly greater in water entering the study area (site 2) than at all other sites. The median values of uranium (14 µg/L) and zinc (20 µg/L) were slightly greater in water leaving the study area (site 14) than in water entering the study area at site 2 (uranium = 7.1 µg/L, zinc = 10 µg/L). The median boron concentration of 480 µg/L in water sampled from a background site (site 13) was greater than the boron concentration of 215 µg/L in water entering the study area (site 2) and the boron concentration of 320 µg/L in water leaving the study area (site 14).

Pesticide concentrations in water were small at all sites and most were less than analytical reporting limits. None of the concentrations measured during the study exceeded available pesticide water-quality criteria or standards.

Specific criteria or standards currently do not exist for assessing the toxic potential of trace-element concentrations in bottom sediment. However, background levels in the Angostura Reclamation Unit lands and throughout the study area are assumed to be represented by geochemical baselines for soils of the Western United States (R.C. Severson, U.S. Geological Survey, written commun., 1987; based on information in Shacklette and Boerngen, 1984). Although not specific to the study area, these baselines are one way of comparing study results to ambient conditions in the Western United States. Analytical results from the bottom-sediment samples obtained during 1988 were compared to these baselines to determine possible elevated concentrations of trace elements in bottom sediment (table 1). Some selenium concentrations were greater than the upper limit of the baseline range. Because most trace-element concentrations were within baseline ranges, there probably is no significant accumulation of trace-element concentrations due to irrigation.

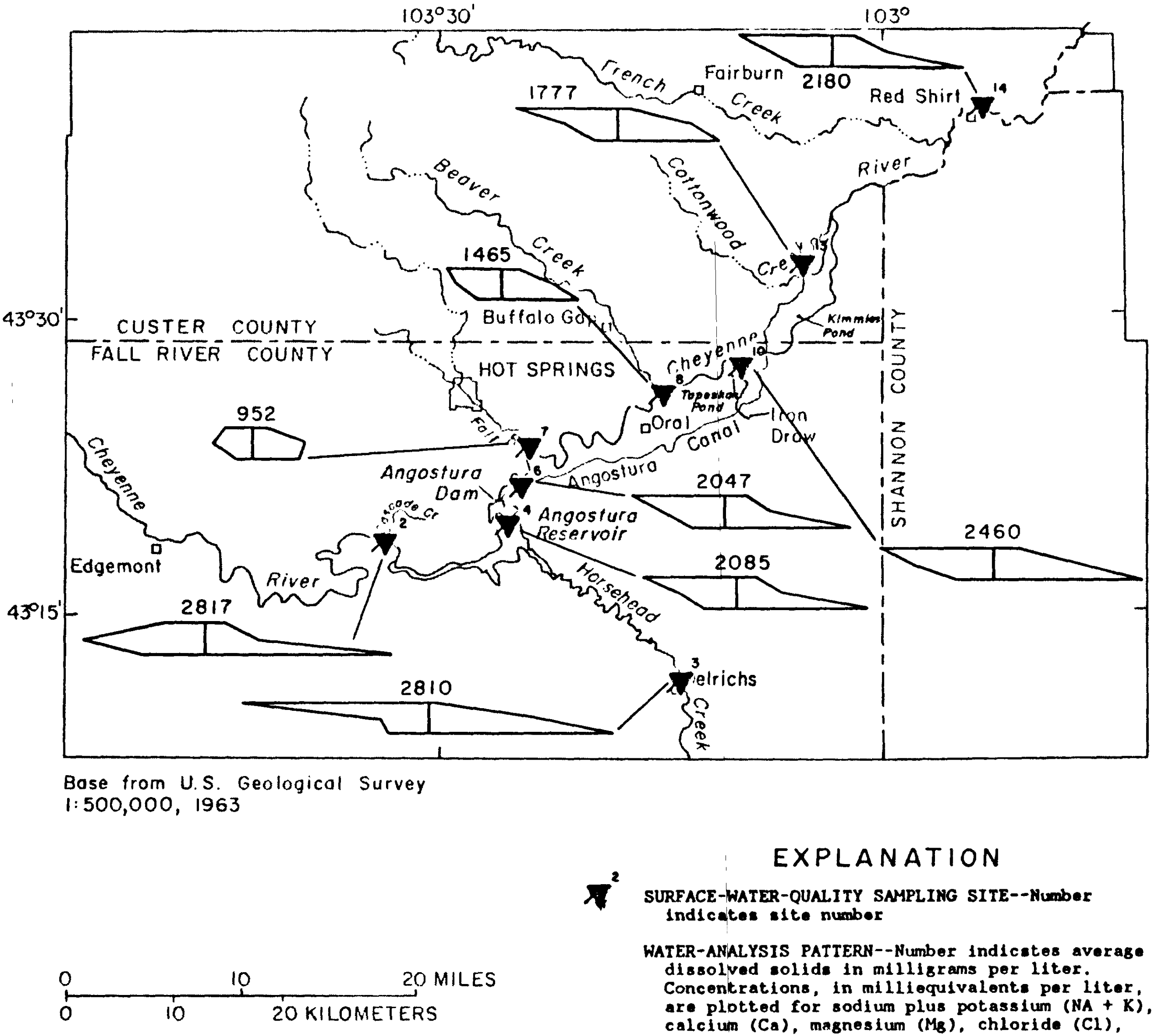
Pesticides, carbofuran and atrazine, were analyzed in samples of bottom sediment from sites where pesticides in water were sampled. Pesticide concentrations in all samples of bottom sediment were less than laboratory analytical reporting limits.

Biota samples for analysis of trace-element concentrations were collected upstream, within, and downstream of the Angostura Reclamation Unit lands. Fish samples were collected during the spring and fall to compare trace-element concentrations in fish influenced by ground-water seepage during the winter and by irrigation return flow during the irrigation season. Aquatic plants and aquatic invertebrates were collected at the same sites as the fish, when possible. Blackbird eggs and other biota were collected at two ponds near the Cheyenne River.

Median concentrations of aluminum in fish were larger upstream of Angostura Reservoir than downstream of the reservoir. Median aluminum concentrations in fish samples collected in April decreased from 352 µg/g (micrograms per gram) at a background site upstream of the reservoir to 73 µg/g at a site near Fairburn, which is downstream of all irrigation return flow. The maximum aluminum concentration in fish was 6,350 µg/g in a sample from the Cheyenne River near Edgemont, upstream of the Angostura Reclamation Unit lands. The maximum aluminum concentrations in invertebrates (7,150 µg/g) and plants (9,370 µg/g) were from a site on the Cheyenne River, midway through the Angostura Reclamation Unit lands, that receives irrigation return flow from upstream irrigated lands. Because of the lack of information on the correlation between aluminum concentrations and biological effects, it is difficult to make inferences in regard to toxicity.

The National Contaminant Biomonitoring Program (NCBP) 85th-percentile baseline value for selenium concentration in fish tissue is 2.8 µg/g dry weight (Lowe and others, 1985; Setmire and others, 1990). Most selenium concentrations in fish tissue sampled were greater than the baseline value at the four sample sites (fig. 5).

Lillebo and others (1988) suggest that the level of selenium residue in whole fish tissue that will adversely affect fish growth or reproduction is 10.0 µg/g (effect level).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French Creek
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Beaver Creek
1465
Buffalo Gap
11
CUSTER COUNTY
FALL RIVER COUNTY
SHANNON COUNTY
Kimmins Pond
Cheyenne
10
HOT SPRINGS
8
Topeshaw Pond
Oral
Iron Draw
952
Fall
7
Canal
Angostura
Angostura Dam
6
2047
Cascade Cr
2
4
Angostura Reservoir
2460
Cheyenne
Edgemont
River
2085
Horsehead
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3
Oelrichs
Creek
2810
0 10 20 MILES
0 10 20 KILOMETERS

Base from U.S. Geological Survey
1:500,000, 1963

EXPLANATION

▼ 2 SURFACE-WATER-QUALITY SAMPLING SITE--Number indicates site number

WATER-ANALYSIS PATTERN--Number indicates average dissolved solids in milligrams per liter. Concentrations, in milliequivalents per liter, are plotted for sodium plus potassium (NA + K), calcium (Ca), magnesium (Mg), chloride (Cl), bicarbonate plus carbonate (HCO_3 + CO_3), and sulfate (SO_4). The anions are plotted to the right of the centerline, and the cations are plotted to the left. The area of the water-analysis pattern is an indication of the dissolved-solids concentration. The larger the area of the pattern, the greater the concentration of dissolved solids

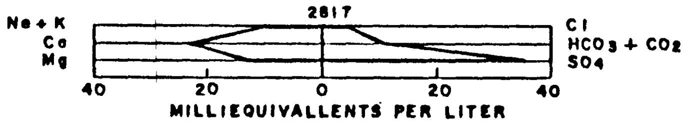
2817
Na + K
Ca
Mg
Cl
HCO3 + CO2
SO4
40
20
0
20
40
MILLIEQUIVALLENTS PER LITER

Figure 3. Chemical quality of water and dissolved-solids concentration at sample sites, 1988.

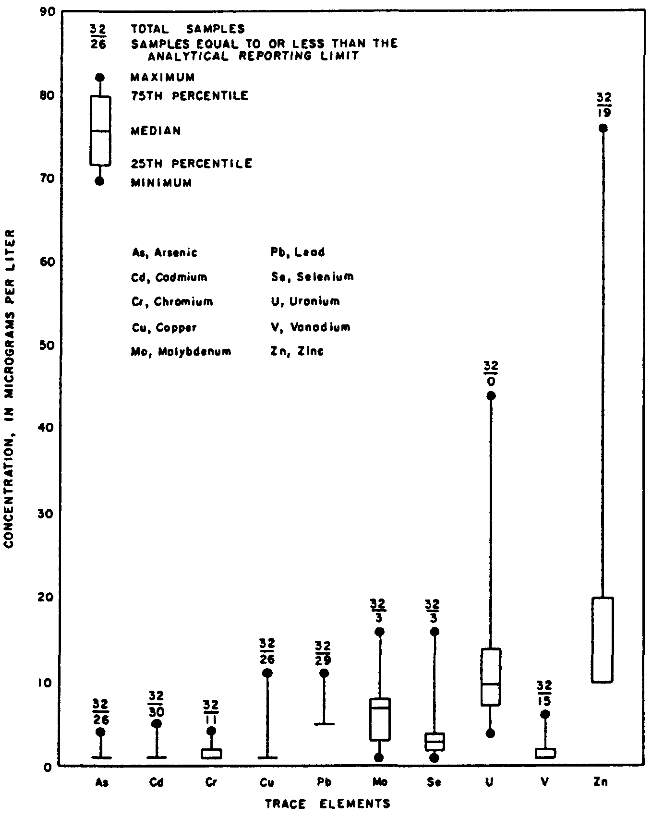

Figure 4. Trace-element concentrations in surface water of the study area, 1988.

Site 5 on the Cheyenne River 0.75 miles downstream of Angostura Dam had the largest median concentration (11 µg/g dry weight). Seven of the nine fish samples collected in September at site 5 had selenium concentrations ranging from 10 to 13 µg/g dry weight. One fish sample collected in April from the Cheyenne River midway through the irrigation Unit (site 12) had a selenium concentration of 10 µg/g dry weight. These values are significant because they equal or exceed the effect level for selenium concentration in fish tissue.

Even though median concentrations of arsenic, copper, and zinc in fish were less than NCBP 85th-percentile baseline values, the concentrations of all three elements exceeded their respective baseline values in a number of individual samples. The median concentrations of these elements during the April and September sampling periods generally were similar at all sites. Concentrations of most other elements in fish were low and are not expected to affect reproduction of fish.

The six fish samples and one blackbird-egg sample that were analyzed for organochlorine pesticides and polychlorinated biphenyls had concentrations either less than analytical reporting limits or very low compared to levels of concern for human consumption. Data from the limited number of samples indicate that pesticide residues are not a problem in biota in the study area.

SUMMARY AND CONCLUSIONS

A study was conducted during 1988 within the Angostura Reclamation Unit and adjacent areas in southwestern South Dakota to determine the concentrations of major ions, selected trace elements, and pesticides in water, bottom sediment, and biota, and to compare the analytical results to various guidelines for environmental protection and to available baseline information.

In general, water in the study area is a sodium sulfate type. Concentrations of trace elements in water delivered to Angostura Reservoir appeared to be similar to irrigation drain water conveyed in return-flow drains, and in the Cheyenne River downstream of the irrigated lands. Pesticide concentrations in water were small at all sites and most were less than analytical reporting limits. The study showed that toxic levels of selenium or other trace elements and pesticides in water probably is not a persistent problem within the study area or downstream of irrigation return flows.

Trace-element concentrations in bottom sediment were very similar to the geochemical baselines for soils of the Western United States, which indicates that there probably is no significant accumulation of trace-element concentrations due to irrigation. Pesticide concentrations in all samples of bottom sediment were less than laboratory analytical reporting limits.

With few exceptions, concentrations of trace elements and pesticides in biota generally were less than values known to produce harmful effects on growth or reproduction. Maximum aluminum concentrations in fish (6,350 µg/g dry weight), invertebrates (7,150 µg/g dry weight), and plants (9,370 µg/g dry weight) were quite large; however, because of the lack of information on the correlation between aluminum concentrations and biological effects, it is difficult to make inferences in regard to toxicity. Selenium concentrations in most whole-body fish tissue samples were greater than the baseline values. Selenium concentrations in seven fish samples at a site upstream from irrigation were near or exceeded levels that could cause detrimental effects. Arsenic, copper, and zinc in biota were present at potentially elevated concentrations in a number of individual samples, but concentrations were not unusually large at any sites and no organisms were present in unusually large numbers. At all sites, pesticide concentrations in biota were small relative to available toxicity data.

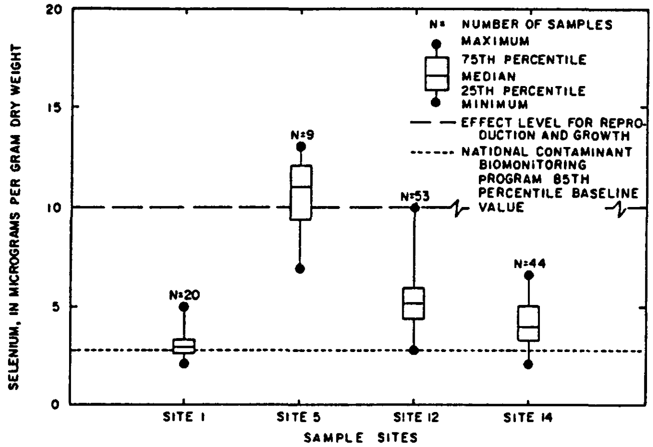

Figure 5. Selenium concentrations in fish tissue from sample sites, 1988.

Table 1. *Comparison of trace-element concentrations in the less than 62-micrometer fraction of bottom sediment in the study area, 1988, and geochemical baselines for soils from the Western United States*

[Total concentration, in micrograms per gram. <, less than; --, no data]

	Bottom sediment		Western soils[1]	
Element	Median	Range	Geometric mean	Baseline range[2]
Arsenic	8.6	6.2 - 15.0	5.5	1.2 - 22
Boron	2.1	1.2 - 7.3	23	5.8 - 91
Cadmium	<2	<2 - 2	--	--
Chromium	57	20 - 85	41	8.5 - 200
Copper	21	8 - 28	21	4.9 - 90
Lead	18	12 - 55	17	5.2 - 55
Mercury	.04	<.02 - .04	.046	.0085 - .25
Molybdenum	<2	<2 - 4	.85	.18 - 4.0
Selenium	1.0	.6 - 14.0	.23	.039 - 1.4
Uranium	2.1	1.9 - 5.3	2.5	1.2 - 5.3
Vanadium	110	31 - 200	70	18 - 270
Zinc	90	39 - 140	55	17 - 180

[1] Modified from Shacklette and Boerngen, 1984.

[2] Range in which 95 percent of sample concentrations are expected to occur.

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PHYSICAL, CHEMICAL, AND BIOLOGICAL PROCESSES IN WATERS AFFECTED BY ACID MINE DRAINAGE: FROM HEADWATER STREAMS TO DOWNSTREAM RESERVOIRS

By Briant A. Kimball[1]

ABSTRACT

Since 1986, the Upper Arkansas River Surface-Water Toxics Project has focused on the geochemistry of metals from acid mine drainage, and on selected aspects of the effects of metals on biological communities. St. Kevin Gulch, near Leadville, Colorado, has been the field site for studying physical, chemical, and biological processes in mountain streams affected by acid mine drainage. Four spatially and temporally intensive sampling efforts in St. Kevin Gulch have tested hypotheses about the process of iron photoreduction, the processes causing metal attenuation dowsntream from acid inflows, the effects of substream flow on metal transport, and the process of phosphorus uptake by algae in iron-rich, acid waters. Other studies have detailed the mineralogy and physical characteristics of hydrous iron oxides to help answer questions about transformations of metals affecting transport in the stream. Biological aspects have included metal uptake by plants, effects of metals on microbiological populations, and pathways for phosphorus uptake by algae. Biological and geochemical aspects of metal transport are combined in the studies of wetland hydrology and metal flux through a wetland at the mouth of St. Kevin Gulch.

Where headwater streams enter the Arkansas River, geochemical processes in mixing zones can transform the metals. Downstream from mixing zones, iron colloids affect the transport of metals over a 250-kilometer reach from Leadville to Pueblo Reservoir. Reservoir sediments that include the colloids and associated metals, represent a temporary endpoint for the metals leaving the Leadville area. Analysis of sediment cores has provided a record of sediment and metal loading from upstream sources.

INTRODUCTION

Acid mine drainage affects hundreds of kilometers of streams in the western United States and in many other areas throughout the world. Remediation of problems caused by acid mine drainage will have a more sound basis if the processes affecting metals in the streams are understood. From 1986 through 1990, the Upper Arkansas Surface-Water Toxics Project has contributed to a broad understanding of metal chemistry related to acid mine drainage by studying physical, chemical, and biological processes throughout the drainage basin (fig. 1).

Primary objectives of the project are to (1) characterize the within-stream processes that control the transport and distribution of selected metals in streams of the Leadville, Colo., area; (2) characterize the chemistry of sediment and sediment coatings that are active in controlling the dissolved concentrations of trace elements; (3) quantify the variability of chemical and hydrologic processes that affect the metals, and (4) quantify processes that affect metal concentrations using reactive-solute transport simulations.

Processes have been studied that occur at different spatial scales, from the small headwater catchment of St. Kevin Gulch, about 4 km (kilometers) long, to about 250 km of the upper Arkansas River basin. This paper summarizes current results, relating the various studies to the project objectives, and describes the continuing objectives of the project.

PROGRESS OF STUDIES

Studies in the upper Arkansas River basin have included detailed work in St. Kevin Gulch, work in the mixing zones where acid water enters the main stem of the Arkansas River, work on the transport of metals downstream from Leadville at the upper end of the drainage basin, and work on the sediments accumulated in Pueblo Reservoir, 250 km downstream from Leadville.

Processes Controlling Transport and Distribution of Metals in a Headwater Stream

St. Kevin Gulch is a headwater stream that begins at the Continental Divide and flows about 4 km before discharging to Tennessee Creek (fig. 2). Past mining in the drainage basin has left tailings piles that add acidic, metal-rich water to the stream. We have used this setting to study the processes that cause spatial and temporal variability of metal concentrations in the stream. Four instream experiments and seasonal, fixed-site sampling have provided data to study processes. In each of the process studies, the chemistry of suspended and bed sediments has been used to evaluate the effect of the solid phases on dissolved concentrations.

Physical processes have been characterized by adding chemical tracers to define discharge, transit time, and transient storage in the stream (Zellweger and others, 1988, 1989; Bencala and others, 1990; Kimball and others, 1991, this Proceedings). Surface- and ground-water interactions also have been studied with the chemical tracers, including an experiment to evaluate streamflow loss to an alluvial fan (Zellweger and others, 1991, this Proceedings), and an experiment to investigate the influence of hillslope hydrology on the mechanics of substream solute storage in gravel-bed streams (Bencala and others, this Proceedings; Harvey and others, 1991, this Proceedings).

Many chemical processes affect metals in acid waters (Chapman and others, 1983; Nordstrom, 1985; Nordstrom and Ball, 1986; Filipek and others, 1987; McKnight and others, 1988). Our work in St. Kevin Gulch has quantified these processes in the context of physical transport of solutes. The interplay between the rate of hydrologic

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[1] U.S. Geological Survey, Salt Lake City, Utah

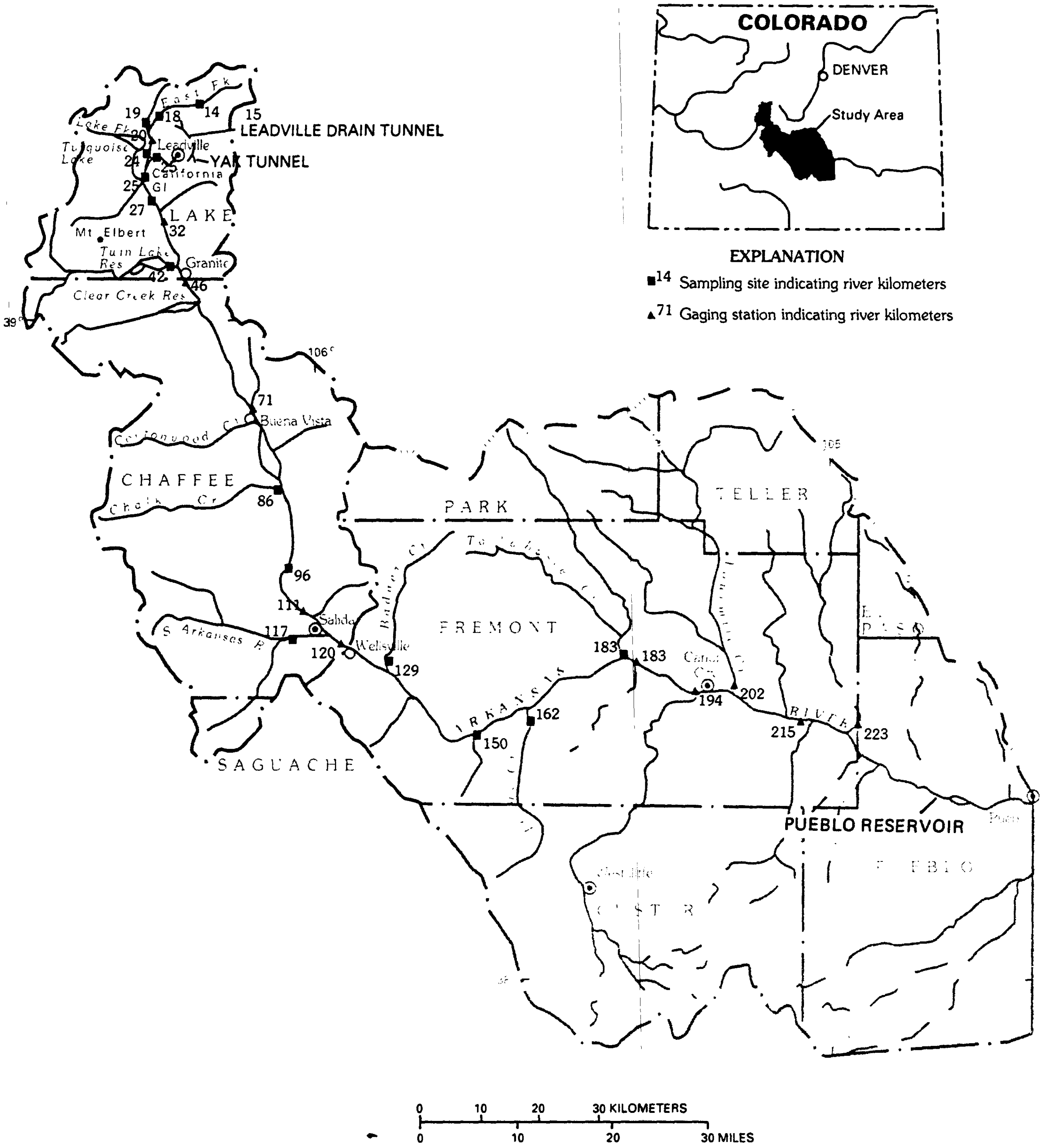
COLORADO
DENVER
Study Area
EXPLANATION
■14 Sampling site indicating river kilometers
▲71 Gaging station indicating river kilometers
East Fk
Lake Fk
Turquoise Lake
19
18
14
15
LEADVILLE DRAIN TUNNEL
20
Leadville
24
23
YAK TUNNEL
California Gl
25
27
LAKE
32
Mt Elbert
Twin Lake Res
Granite
42
46
Clear Creek Res
39°
106°
71
Buena Vista
Cottonwood Cr
CHAFFEE
Chalk Cr
86
PARK
TELLER
96
111
Salida
S Arkansas R
117
120
Wellsville
129
FREMONT
SAGUACHE
ARKANSAS
150
162
183
183
194
202
RIVER
215
223
PUEBLO RESERVOIR
0 10 20 30 KILOMETERS
0 10 20 30 MILES

Figure 1. Location of study area indicating sampling sites in the upper Arkansas River basin.

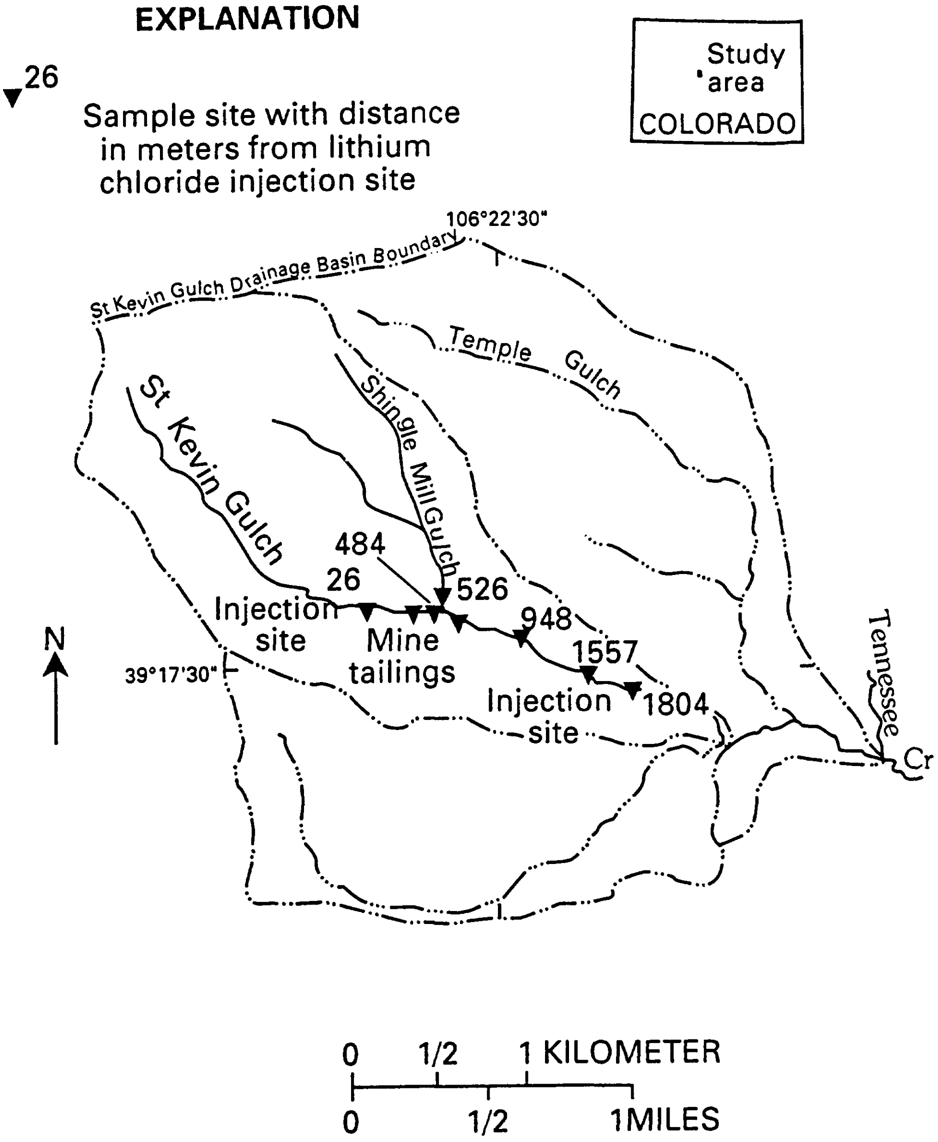
EXPLANATION
26
Sample site with distance in meters from lithium chloride injection site
Study area
COLORADO
106°22'30"
St Kevin Gulch Drainage Basin Boundary
Temple Gulch
St Kevin Gulch
Shingle Mill Gulch
484
26
526
948
1557
1804
Injection site
Mine tailings
Injection site
Tennessee Cr
N
39°17'30"
0 1/2 1 KILOMETER
0 1/2 1 MILES

Figure 2. Location of sampling sites in St. Kevin Gulch.

transport and rates of chemical reactions influences solute concentrations in streamwater. The magnitude of chemical processes varies in time and space. Our sampling has been spatially detailed to evaluate the processes affecting metals downstream from acidic inflows. These have included advection, laterial inflows, and chemical reactions, all of which have been simulated in steady-state solute-transport models (Kimball and others, 1988; Kimball and others, 1991, this Proceedings).

Sampling to define temporal variations has indicated that photoreduction of iron is a diel processes affecting iron speciation and concentration in the stream (McKnight and others, 1988; Kimball and McKnight, 1989). We have sampled for diel variations in the substream zone to see whether the in-stream diel variations are affected by process in the subsurface. Variations in pH affect almost all the metals, causing changes in speciation, formation of colloids, and precipitation. These reactions have been examined in a pH-perturbation experiment to study kinetics of metal reactions in response to changing environmental conditions (Kimball and others, 1990). For both spatial and temporal scales, we have quantified the major processes and their variability (Bencala and McKnight, 1987).

Studies of chemical processes in St. Kevin Gulch range from stream-scale processes discussed above to processes that occur on the molecular scale. The equilibrium partitioning of metals between water and sediment is a molecular-scale process that can be investigated in the context of a chemical equilibrium model (Smith and others, 1989; Smith and others, 1991, this Proceedings). The molecular mechanism of iron photoreduction includes the production of an hydroxyl radical (Sigleo and others, 1988).

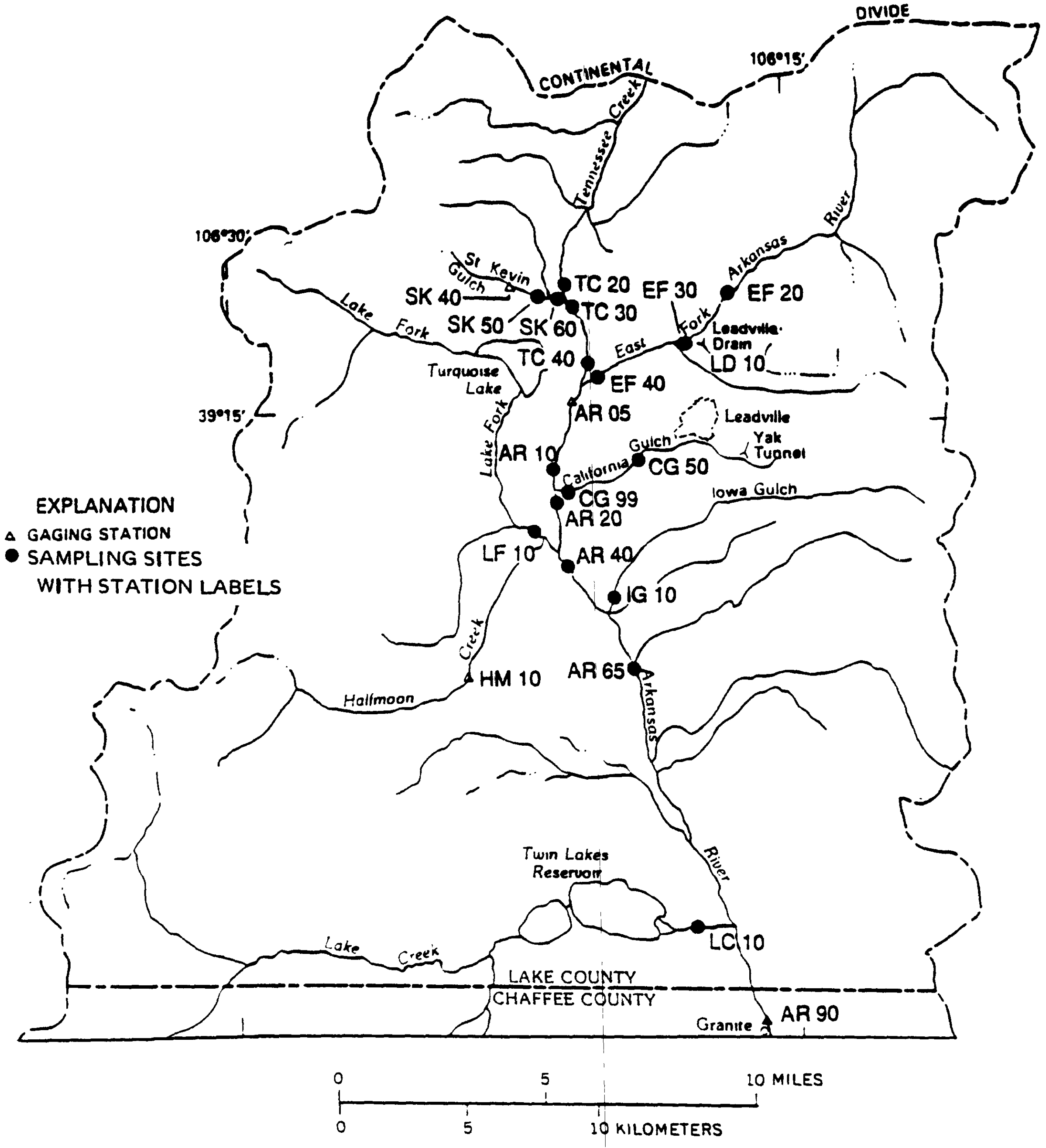
CONTINENTAL DIVIDE
106°15'
106°30'
39°15'
Tennessee Creek
St Kevin Gulch
Lake Fork
SK 40
SK 50
SK 60
TC 20
TC 30
TC 40
EF 30
EF 20
EF 40
Arkansas River
East Fork
Leadville Drain
LD 10
Turquoise Lake
AR 05
Leadville
Yak Tunnel
AR 10
California Gulch
CG 50
CG 99
AR 20
Iowa Gulch
LF 10
AR 40
IG 10
Halfmoon Creek
HM 10
AR 65
Arkansas River
Twin Lakes Reservoir
LC 10
Lake Creek
LAKE COUNTY
CHAFFEE COUNTY
Granite
AR 90
EXPLANATION
▲ GAGING STATION
● SAMPLING SITES WITH STATION LABELS
0
5
10 MILES
0
5
10 KILOMETERS

Figure 3. Location of mass balance sampling sites.

Also on the molecular scale, the relation of dissolved organic matter to the surface charge of iron hydroxide particles has been studied by observing the seasonal changes in electrophoretic mobility of particles (Ranville and others, 1989; Ranville and others, 1991, this Proceedings).

Biological processes in acidic waters are not well understood, and the diversity of the stream ecosystem is limited in acid waters (McKnight, 1988). Two biological experiments have been conduced in St. Kevin Gulch. The toxicity of metals on microbiological populations was tested on organisms that had been grown on artificial substrates in the stream (Sharon Berk, Tennessee Technical University, written commun., 1988). The pathways of phosphorus uptake by algae have been followed by a controlled release of ^{32}P (Tate and others, 1991, this Proceedings). The uptake of metals by plants along St. Kevin Gulch and in the wetland has been described (Erickson, 1989; Erickson and others, 1991, this Proceedings). Processes that control water quality in a subalpine wetland receiving acid mine drainage have been identified at the mouth of St. Kevin Gulch (Walton-Day and Briggs, 1989; Walton-Day and others, 1991, this Proceedings).

Processes in Mixing Zones of Streams Affected by Acid Mine Drainage and the Arkansas River

Mixing zones develop where streams affected by acid mine drainage discharge to the Arkansas River. We have developed a network of sites to sample water from mixing zones to observe the temporal and spatial variability of processes (fig. 3). The approach is to calculate the mass balance of metals through mixing zones (Bencala and McKnight, 1987, Bencala and others, 1987).

Calculation of metal loads in streams can be difficult or inaccurate when traditional methods are applied (Nordland and Kimball, 1989). Concentrations of major constituents in streamwater generally have an inverse correlation to discharge, and discharge alone is an adequate predictor of solute loads. Because a large number of environmental factors influence the instantaneous concentration of metals in streamwater, metals generally have a much less defined relation to discharge. These environmental factors include variable contributions from point sources of metals, variable pH and redox conditions, the type and quantity of complexing agents, fluctuations in sediment concentration, biological activity, and temperature (Forstner and Wittmann, 1979).

Because the task of predicting metal concentration and, subsequently, metal loads is complex, another objective of the Upper Arkansas River Surface-Water Toxics Project has been to define the key factors contributing to metal loads (Wetherbee and Kimball, 1991, this Proceedings). Physical and chemical variables have been measured over a range of conditions to provide a data base from which statistical relations between metal loads and environmental variables can be evaluated.

Downstream from mixing zones, colloidal iron plays an important part in metal transport (Bencala and others, 1988; Kimball and Wetherbee, 1989). Sediment-water interactions have been addressed by sampling at sites downstream from Leadville to Pueblo Reservoir (Callender and others, 1991, this Proceedings). Analysis of bed-sediment cores from Pueblo Reservoir have indicated the possibility of deposition from large, historic discharges from the Yak Tunnel at Leadville (Callender and others, 1989).

Processes of Water-Sediment Interaction in Pueblo Reservoir

Our interest in Pueblo Reservoir has been its role in accumulating metal-rich sediments and the transformation or diagenesis of those sediments (Callender and others, 1989). Cores from the reservoir provide about 10 years of record of sediment discharge. Another point of interest has been the characterization of organic colloids and suspended particulates in Pueblo Reservoir (McKnight and others, 1991, this Proceedings).

DIRECTION OF FUTURE STUDIES

The Upper Arkansas River Surface-Water Toxics Project has been oriented toward understanding processes, quantifying their magnitude and variability, and simulating these processes in reactive solute-transport models. During the next 3 years, the project efforts will include (1) Development of solute transport simulations to understand and quantify processes; (2) definition of mass balance of processes in mixing zones of the Arkansas River; (3) investigation of the transport and transformation of metals in the Arkansas River, particularly as affected by seasonal variations in flow and water chemistry; and (4) transformation or diagenesis of Arkansas River sediment during storage in Pueblo Reservoir.

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USE OF MASS-FLOW CALCULATIONS TO IDENTIFY PROCESSES CONTROLLING WATER QUALITY IN A SUBALPINE WETLAND RECEIVING ACID MINE DRAINAGE, ST. KEVIN GULCH, COLORADO

By Katherine Walton-Day[1], Paul H. Briggs[1], and Samuel B. Romberger[2]

ABSTRACT

This paper presents preliminary mass-flow calculations for iron, copper, cadmium, zinc, and manganese in surface water flowing through a subalpine wetland affected by acid mine drainage near Leadville, Colorado. Instantaneous mass-flow calculations for June 1, June 20, and July 11, 1988, indicate iron and copper were being removed from surface water by the wetland on the former two dates. Cadmium and zinc were flushed from the wetland on June 1 and exhibited conservative behavior (that is, mass inflow equaled mass outflow) on June 20. Manganese, however, behaved conservatively on June 1 but was flushed from the wetland on June 20. Mass inflows of the five metals were greater than outflows on July 11. These patterns are enhanced by complications in the surface-water hydrology of the wetland at that time and are, therefore, not definitive. Processes causing metal removal by the wetland include the formation and precipitation of iron oxyhydroxide material and the pH-controlled sorption of copper.

INTRODUCTION

Constructed and natural wetlands have been investigated as passive treatment facilities for acid mine drainage resulting from coal and base- and precious-metal mining (for example, Wieder and Lang, 1984; Dollhopf and others, 1988; Hammer, 1989; Machemer and others, 1990). Wetlands remove some contaminants from influent mine drainage by a variety of processes, including microbially mediated sulfate reduction and accompanying sulfide precipitation, metal-oxide formation, and metal-organic interactions.

This paper presents preliminary mass-flow calculations for iron, copper, cadmium, zinc, and manganese for three periods during and following 1988 spring runoff in a natural subalpine wetland. These results can be used to assess whether the wetland improves the water quality of acid mine drainage flowing through the wetland, and what processes cause measured water-quality improvements.

METHODS

The field site is a 26-hectare subalpine wetland located about 7 km (kilometers) northwest of Leadville, Colo. (fig. 1). Five streams, Temple Gulch, Gleason Gulch, North Spring, South Spring, and St. Kevin Gulch, discharge into the wetland, which has one outlet. The principal source of acid mine drainage to the wetland is St. Kevin Gulch, which receives drainage from mine tailings about 1.5 km upstream from the wetland. The pH of St. Kevin Gulch near the wetland is about 3.5 to 4.0, and the streamwater contains concentrations of iron, manganese, and zinc in milligrams per liter and cadmium and copper in micrograms per liter (McKnight and others, 1988).

The field site was instrumented with continuously recording Parshall flumes at the five inflow sites and a continuously recording streamflow gage at the outflow site (fig. 1). The error of Parshall flume measurements is reported as 5 percent (Winter, 1981). Independent measurements of flow by current meter and 3-in. (inch) Parshall flumes at the inflow sites and by 3-in. Parshall flumes at the outflow site generally confirmed this range of error for the flumes but indicated as much as 10-percent error for the recording streamflow gage. Several flumes are located upstream from the wetland boundary because stream-channel morphology prevented flume installation closer to the wetland (fig. 1).

Water-quality samples were collected at the six surface-water sites on June 1, June 20, and July 11, 1988. Temperature, pH, specific conductance, and dissolved-oxygen concentration were measured onsite by methods described in Walton-Day and others (1990).

Metal concentrations were measured by inductively coupled plasma-atomic emission spectrometry (Lichte and others, 1987) on unfiltered, acidified samples, and on filtered (0.1-µm (micrometer)) acidified samples. Bicarbonate ion concentrations were determined on unfiltered, unacidified samples using a gran titration (Stumm and Morgan, 1981) within 10 hours of sample collection. Sulfate, chloride, fluoride, and nitrate concentrations were determined on filtered, unacidified samples using ion chromatography (Fishman and Pyen, 1979). Total organic carbon was measured on unfiltered, unacidified samples as described in Wershaw and others (1987). Charge balances, duplicate sample analyses, and analyses of standard reference samples indicated the analyses to be accurate to ± 10 percent.

Quantifying the mass flow of a solute in a natural system requires identification and measurement of all inputs and outputs of the solute. In this wetland, inflows of solute include surface-water flow, ground-water flow, and precipitation; outflows are surface- and ground-water flow. Mass flow is calculated by multiplying the stream discharge, in liters per second, by the concentration of a water-quality constituent in milligrams per liter, which yields mass flow (also known as constituent discharge), in milligrams per second. A simplified equation representing the mass flow of any component then is:

$$\sum (Q \times C)\text{inputs} - \sum (Q \times C)\text{outputs} = \text{Net Mass Flow}$$

where Q is the flow and C is the concentration of the constituent. In this paper, precipitation was neglected because no precipitation occurred during sampling. In addition, the

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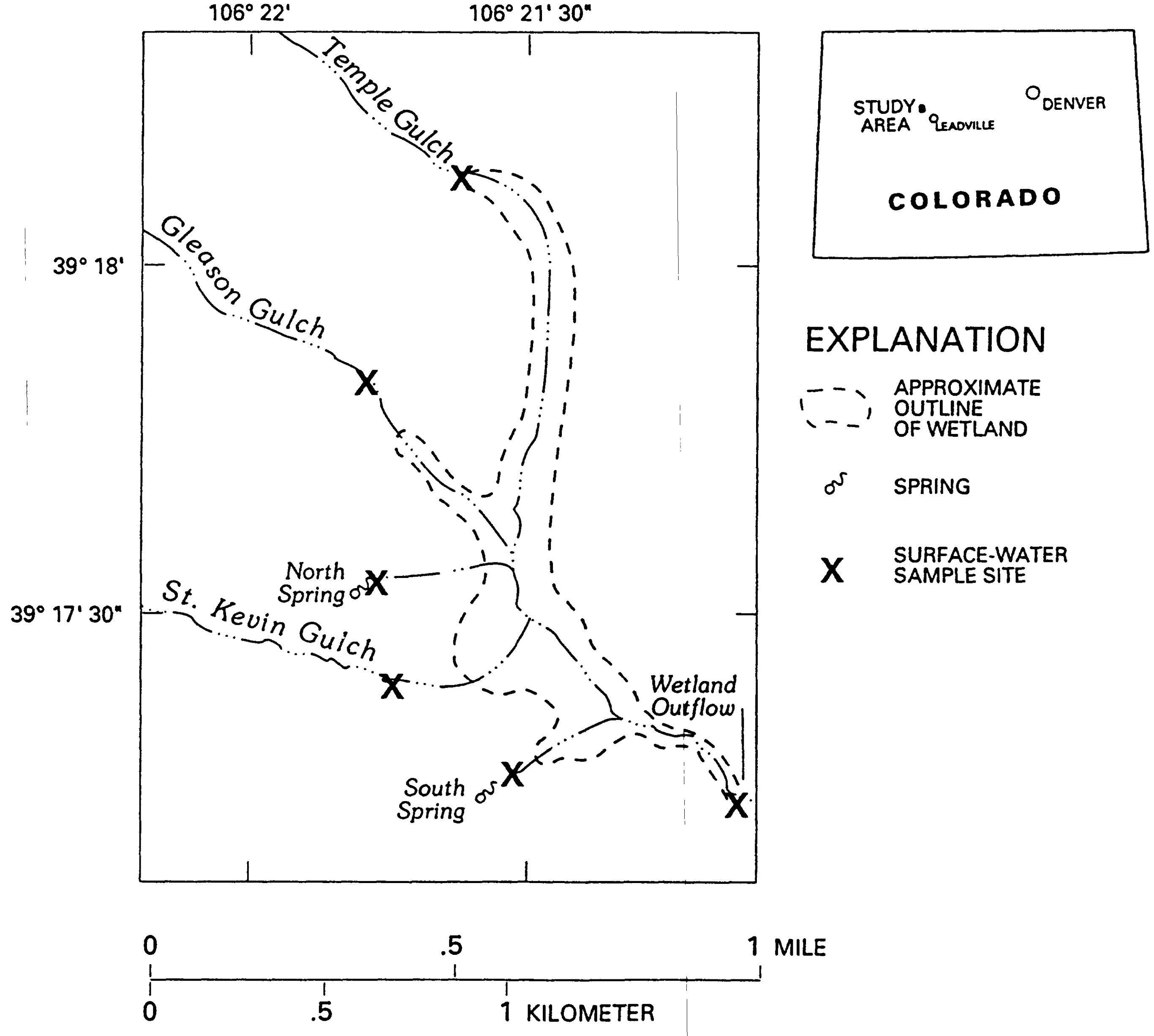
106° 22'
106° 21' 30"
39° 18'
39° 17' 30"
Temple Gulch
Gleason Gulch
North Spring
St. Kevin Gulch
Wetland Outflow
South Spring
STUDY AREA
LEADVILLE
DENVER
COLORADO
EXPLANATION
APPROXIMATE OUTLINE OF WETLAND
SPRING
X SURFACE-WATER SAMPLE SITE
0
.5
1 MILE
0
.5
1 KILOMETER

Figure 1. Location of study area. (Modified from Walton-Day and Briggs, 1989).

contribution of ground water to the mass-flow equation is not included. Preliminary calculations indicate that ground-water flow represents less than 10 percent of the flow in the wetland during the spring-runoff period, and that the ground-water mass flow of the elements considered here is minor (Katherine Walton-Day, 1989, unpublished data on file with the U.S. Geological Survey, Denver, Colo.).

RESULTS AND DISCUSSION

Hydrology

If all the flow components of interest have been accounted for in the wetland, the water balance for the wetland should show closure within the error margin of the measurement techniques. The water balance for the wetland excludes precipitation, evapotranspiration, ground-water flow, and change in storage in the wetland. Surface-water flow is assumed to dominate the hydrologic balance of the wetland during spring runoff.

The surface-water balance for the wetland for the three sampling periods is shown in figure 2. Inflows balance the outflow for the June 1, 1988, sampling within the range of measured error (± 10 percent). However, for the other two sampling periods, surface-water inflows to the wetland do not balance the outflow.

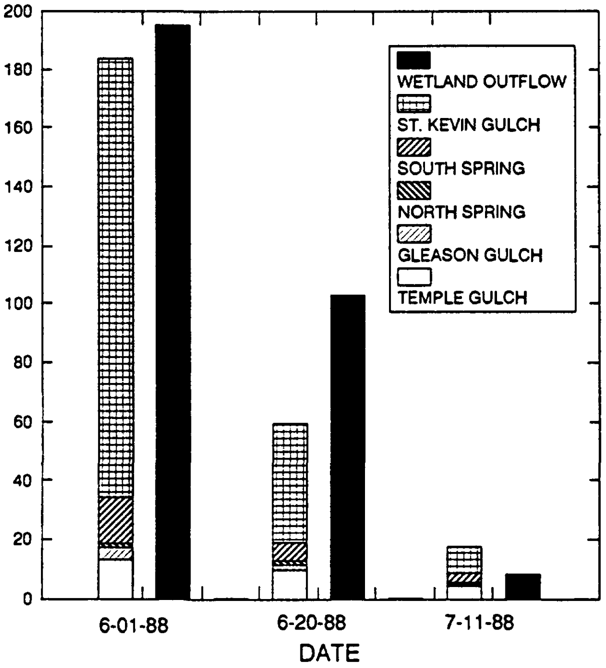

Figure 2. Surface-water balance for the wetland for the three sampling periods.

The surface-water balance for June 20 shows that outflow greatly exceeded inflows (fig. 2). Detailed hydrographs for the St. Kevin Gulch inflow and the wetland outflow for June 19-21, 1988, are shown in figure 3. The St. Kevin Gulch hydrograph indicates that storms occurred on June 19 and 20. The wetland outflow had a delayed response to the storms and a much slower return to prestorm flow conditions than did the St. Kevin Gulch inflow. This delayed response resulted from detention storage of stormwater in the wetland and a longer residence time (because of lower flow rates) of water in the wetland on June 20 than on June 1. Therefore, on June 20, the surface-water terms of the flow equation do not balance because sampling occurred when the discharge of the five inflow streams, represented by the St. Kevin Gulch inflow, had returned to prestorm conditions, but flow at the wetland outflow was elevated because of the June 19 storm.

The surface-water balance for July 11 shows that inflows exceeded outflow. There are at least two explanations for this imbalance. The first explanation is failure to include evapotranspiration in the instantaneous water balance. This omission has no effect on the calculation of mass flow because evapotranspiration does not remove soluble components. The second explanation is that not all flow recorded at the inflow sites enters the wetland. In particular, observations and measurements at the St. Kevin Gulch inflow indicate that the stream reach between the Parshall flume and the wetland boundary is a losing reach during the low-flow conditions that prevail after snow-melt runoff ends. In addition, the region of the wetland fed by Temple Gulch, north of Gleason Gulch, can become hydrologically isolated from the rest of the wetland during low-flow conditions--that is, as the water table falls, a subtle surface-water divide forms in the wetland so that water from Temple Gulch flows into a stagnant basin and evaporates.

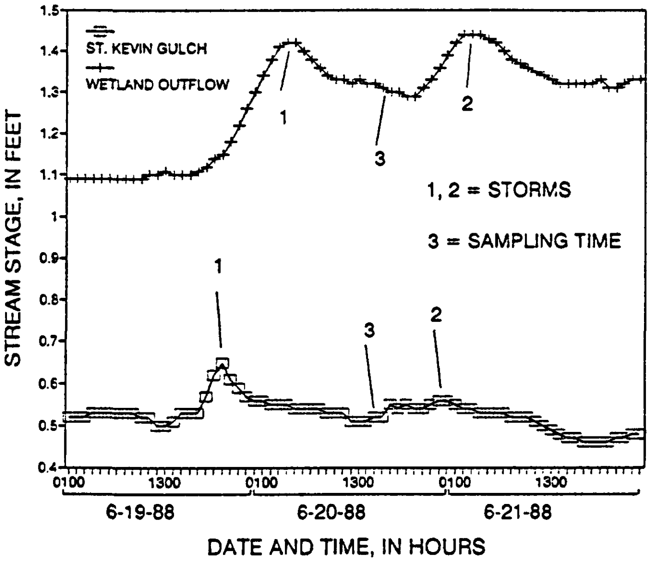

Figure 3. Hydrographs for St. Kevin Gulch inflow to the wetland and the wetland outflow for June 19-21, 1988.

Mass-Flow Calculations

With an understanding of the problems inherent in instantaneous water balances for the wetland, the corresponding mass-flow calculations can be interpreted. Mass flows calculated on the basis of analyses of unfiltered water samples for iron, copper, cadmium, zinc, and manganese for the three sampling periods are shown in figures 4 and 5.

The June 1 and 20 data clearly indicate removal of both iron and copper from the water by the wetland. The amount of removal indicated on June 1 exceeds the combined errors of the flow and water-quality determinations (about ± 20 percent). Iron removal is evident on June 20, although the amount of copper removed approaches the uncertainty of the measurements. The July 11 data indicate loss of iron and copper to the wetland, but uncertainties in the water budget weaken this conclusion.

The cadmium, zinc, and manganese data indicate possible removal of these elements only for the July 11 sampling date (fig. 5). Cadmium and zinc were flushed from the wetland during the high-flow conditions on June 1. On June 1, the difference between the manganese inflows and outflow was within measurement errors; manganese behaved conservatively. Conservative behavior is defined herein as mass inflow equals mass outflow. The June 20 data indicate flushing of manganese and conservative behavior of cadmium and zinc. However, because of the imbalance of the hydrologic budget, these conclusions are uncertain. The July 11 data indicate possible removal of all three elements by the wetland.

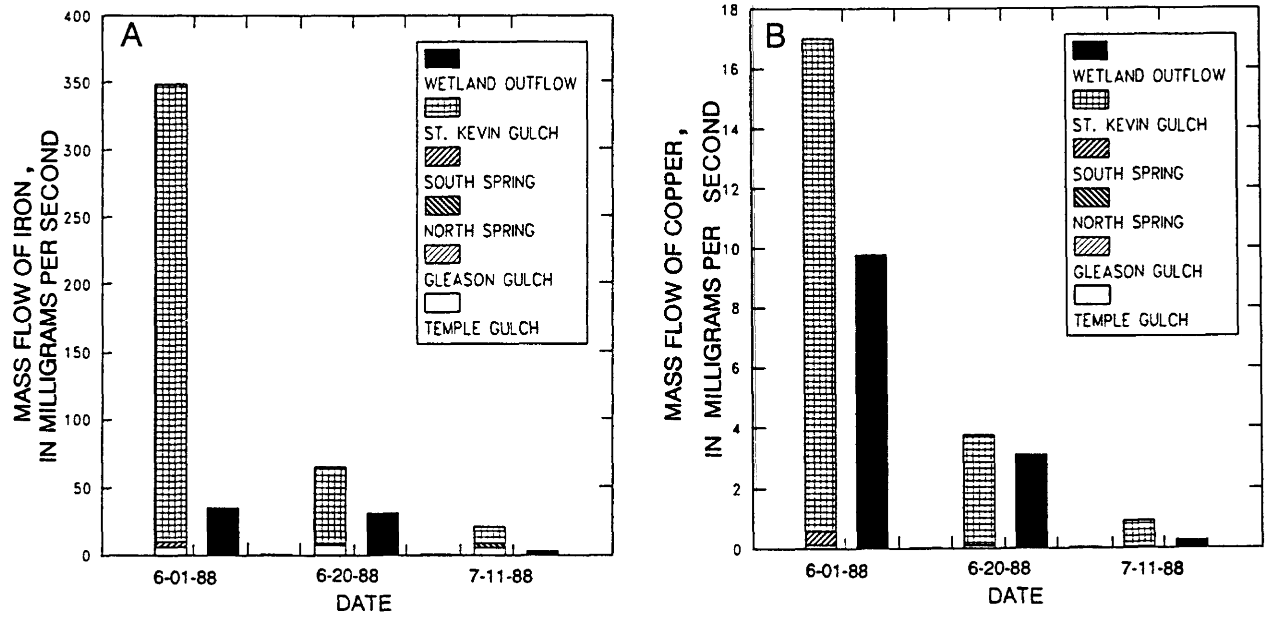

Figure 4. Calculated mass flows of iron (A) and copper (B) for the three sampling periods.

Processes Causing Metal Removal

The removal of iron most likely is caused by the formation and settling of iron oxyhydroxide flocculent material. Comparisons of mass-flow calculations for unfiltered and filtered samples indicate a decrease in the quantity of iron removed from the wetland with filtration. For instance, for the June 1 data, 175 mg/s (milligrams per second) of iron flowed into the wetland, and 25 mg/s of iron flowed out, indicating removal of 150 mg/s of iron by the wetland (compare with data for the unfiltered sample (fig. 4), which indicates removal of more than 300 mg/s). These data indicate that iron traveled through the wetland in dissolved and particulate form, and that both forms were removed from water by the wetland.

Formation and precipitation of iron oxyhydroxide flocculent has been documented in St. Kevin Gulch upstream from the wetland (Kimball and others, 1988). In addition, site observations indicate visible accumulations of iron flocculent where St. Kevin Gulch discharges into the wetland. The formation and settling of this material are responsible for the observed removal of iron by the wetland.

Other possible removal mechanisms for iron include sorption or complexation with organic material and formation of iron sulfides. The former cannot be evaluated with this data set, and lack of evidence of sulfate removal by the wetland discounts the latter. Mass-flow calculations for sulfate for the three sampling periods are listed in table 1. Sulfate was conserved on June 1, was flushed from the wetland on June 20, and may have been removed on July 11. However, the uncertainty of data from this sampling period has been discussed previously. Therefore, the formation of iron oxyhydroxide flocculent most likely controls the removal of iron from surface water by the wetland.

Sorption of copper onto wetland sediments was the most likely process controlling its removal by the wetland during the 1988 runoff. Copper mass-flow calculations do not indicate strong variations between filtered and unfiltered samples, indicating that dissolved (<0.1-µm) copper is the dominant form of copper removed by the wetland. The pH of wetland sediments generally increases downstream from St. Kevin Gulch (unpublished data on file with the U.S. Geological Survey, Denver, Colo.). Laboratory titrations of iron flocculent material collected upstream in St. Kevin Gulch have indicated pH-controlled removal of copper from solution by sorption to iron oxyhydroxides (Smith and others, 1991, this Proceedings). The sulfate mass-flow calculations do not support formation of sulfide minerals as a removal mechanism. Complexation of copper by organic matter cannot be evaluated with this data set.

The calculated flush of cadmium, zinc, and manganese from the wetland is problematic. The concurrent flushing of total organic carbon (table 1), and a transformation of the three metals from a mixture of dissolved and particulate material at the inflows, to predominantly dissolved material at the outflows (unpublished data on file with the U.S. Geological Survey, Denver, Colo.) indicate the formation of dissolved metal-organic complexes during passage through the wetland. However, uncertainty in the mass-flow calculations for these elements prevents any firm conclusions regarding processes controlling their behavior.

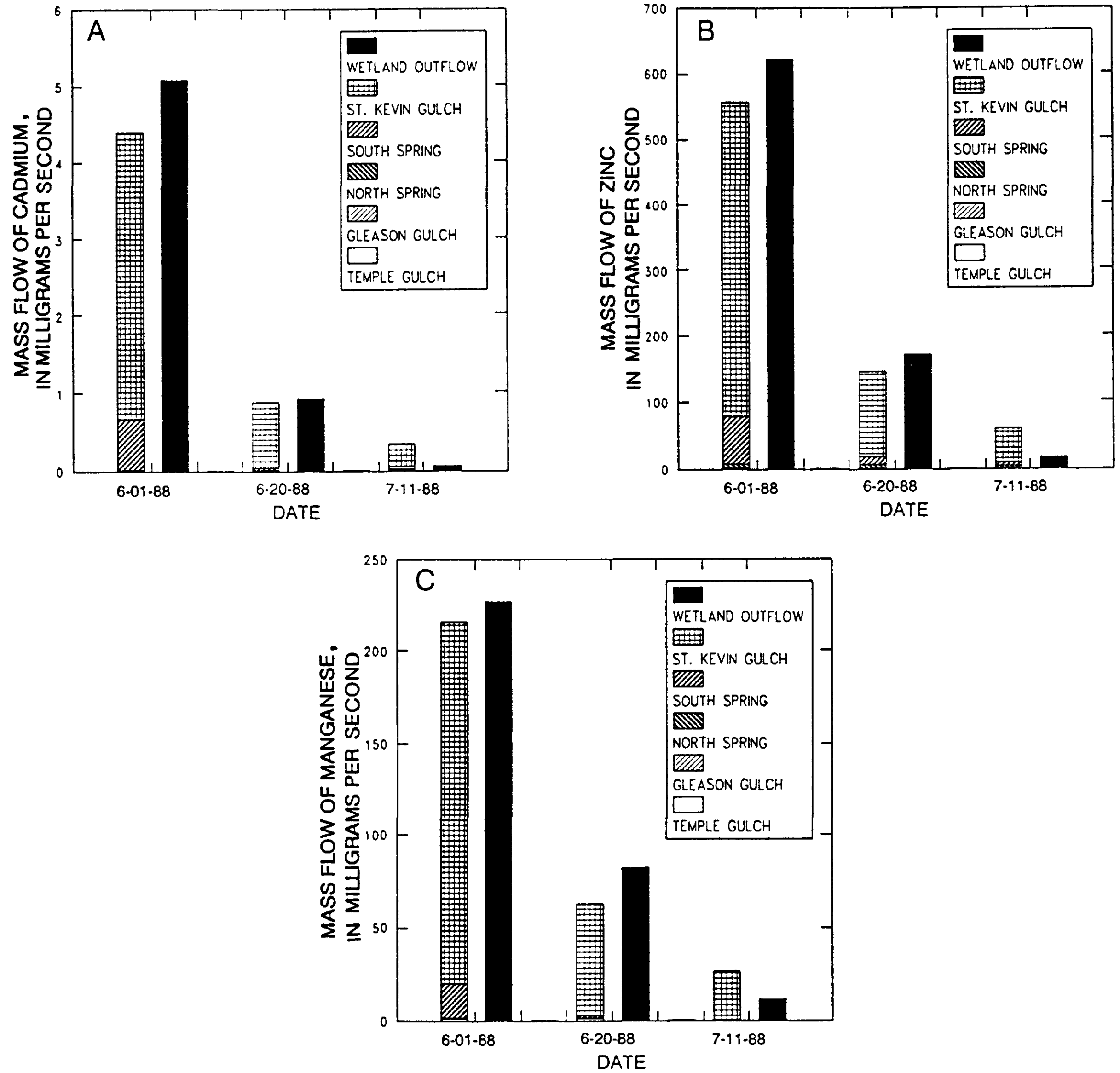

Figure 5. Calculated mass flows of cadmium (A), zinc (B), and manganese (C) for the three sampling periods.

Table 1. *Mass-flow calculations for sulfate and total organic carbon*

[mg/s, milligrams per second; net = inflow-outflow; a negative value for net indicates flushing of the constituent from the wetland; a positive value indicates deposition of the constituent in the wetland]

	Sulfate mass flow (mg/s)			Total organic-carbon mass flow (mg/s)		
Date	Inflow	Outflow	Net	Inflow	Outflow	Net
6-01-88	7,790	8,280	-490	350	490	-140
6-20-88	2,240	3,410	-1,170	110	590	-480
7-11-88	970	471	499	25	26	-1

CONCLUSIONS

Mass-flow calculations indicate removal of iron and copper from surface water by a subalpine wetland receiving acid mine drainage on June 1 and June 20, 1988. Cadmium and zinc were flushed from the wetland during high-flow conditions on June 1, but manganese was conserved. Conversely, on June 20, cadmium and zinc were conserved and manganese was flushed from the wetland. The June 20 trends are biased by the timing of sampling relative to the stream hydrographs; mass outflows are enhanced because the outflow was sampled during the latter part of a storm hydrograph. The July 11 data indicate removal of all five elements by the wetland, but this conclusion is uncertain because of problems in defining the hydrologic budget for this sampling period.

The most likely processes responsible for iron and copper removal are formation and settling of iron oxyhydroxide flocculent and sorption, respectively. Mass-flow calculations indicate that sulfate is being flushed from the wetland, and, therefore, sulfide reduction is not indicated. Cadmium, zinc, and manganese may form dissolved metal-organic complexes during passage through the wetland.

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USE OF VARIATION IN SOLUTE CONCENTRATION TO IDENTIFY INTERACTIONS OF THE SUBSTREAM ZONE WITH INSTREAM TRANSPORT

By Kenneth E. Bencala[1], Briant A. Kimball[2], Diane M. McKnight[3]

ABSTRACT

In St. Kevin Gulch (upper Arkansas River basin; Leadville, Colorado), a reconnaissance study was conducted to identify hydro-chemical interaction of the substream zone with instream transport. Acid mine drainage causes several trace metals to be present at elevated concentrations relative to those typical of pristine Rocky Mountain streams. The reconnaissance was an adjunct to an experimental study of trace-metal retention within the streambed.

In streams that receive acid mine drainage, instream alterations of concentrations of various solutes can occur episodically. The primary experiment included maintenance of steady instream lithium concentration above background level, sharp changes in sodium concentration, and adjustments of pH sufficient to cause variations in copper concentration. Four shallow, open "wells" in the substream zone adjacent to the stream channel were sampled.

Lithium and sodium concentrations were interpreted to identify a definite, highly variable, hydraulic connection between the substream zone and the stream channel. In this reconnaissance study, copper concentrations varied within the substream zone; however, the variations could not be related to the experimentally induced instream variations. Thus, the coupled hydrochemical interaction of the substream zone with instream solute transport may differ among solutes.

INTRODUCTION

Direct observations of interactions of the substream zone with instream transport have been made at only a limited number of streams. Perhaps the most extensively documented site has been Little Lost Man Creek, Humboldt County, Calif. (Bencala and others, 1984). In Little Lost Man Creek, month-long observations of stream and substream solute transport have shown that the substream zone temporarily stores solutes by physical and chemical processes. This phenomenon of transient storage in the substream zone has the effect in the stream of delaying solute arrival, attenuating solute peak concentrations, and extending solute residence time.

In addition to the direct observations in Little Lost Man Creek, information from several perspectives has indicated that interactions with the substream zone may have significance in understanding toxic substance transport in contaminated streams. Observations of instream data in Uvas Creek, Santa Clara County, Calif. (Jackman and others, 1984) and in the Snake River, Summit County, Colo. (Bencala and others, 1990) have been interpreted by use of transport simulations, to infer the occurrence of transient storage in substream zones. In a stream at Oak Ridge National Laboratory, Tenn., Cerling and others (1990) have interpreted the retention of a radionuclide within the depth profile of the streambed as an indication of significant underflow. A simulation study (Kim and others, 1990) of transport experiments conducted in a flume with nitrate have further indicated that transient storage in substream zones may influence concentrations of reacting solutes.

Procedures to identify interactions of the substream zone with instream transport are largely experimental and without generally accepted protocols. The purpose of the study described herein is to assess whether or not these interactions existed in St. Kevin Gulch. As experimental solute injections were already in progress, the reconnaissance study was conducted subject to the experimental and sampling limitations imposed by the ongoing studies at the site (Kimball and others, 1990).

St. Kevin Gulch is an acidic mountain stream. McKnight and others (1988) have presented the background site information. As they described, hydrous iron oxides are abundant on the streambed, and ambient chemical variations of the stream system occur on a daily cycle. In the summer of 1988, several solute injection experiments were conducted to study trace-metal retention associated with streambed hydrous iron oxides. As a consequence of these injections, the concentrations of three solutes (lithium, sodium, and copper) were available to be reviewed to identify interactions of the substream zone with instream transport.

The study zone was an approximately 70-m (meter)-long reach of the stream (fig. 1). Along this reach,

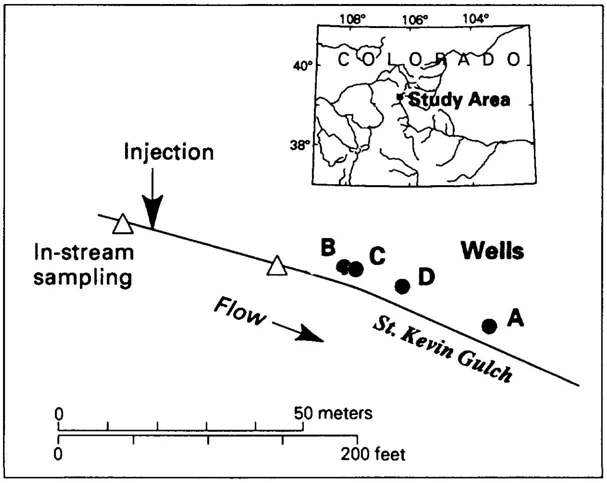

Figure 1. Location of study area shown in insert. In the sketch of the site, triangles indicate in-stream sampling sites and circles indicate sites of the shallow wells.

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[1] U.S. Geological Survey, Menlo Park, Calif.

[2] U.S. Geological Survey, Salt Lake City, Utah

[3] U.S. Geological Survey, Denver, Colo.

about 30 cm(centimeter) from the stream edge, four sampling pits were dug about 20 cm deep into the surrounding soil. Sites for the sampling pits were selected entirely on pragmatic, physical considerations, including ease of access by personnel engaged in the primary experiment, and avoiding cobbles and boulders. (These sampling pits are referred to herein as "wells.") Approximately 1 km (kilometer) above the study zone, lithium was steadily injected into the stream for several days before and continuing through the sampling discussed herein. Approximately 10 m above the study zone, sodium was injected continuously into the stream in successive additions for two periods lasting 3 hours each. The pH of the stream through the study zone also was adjusted during each of these 3-hour periods (first from pH 3.5 to pH 4.2, and then to pH 5.8). As the pH approached 5.5, copper concentration decreased in the stream. Chapman (1982) published results that showed a decrease of copper concentration following an experimental increase of stream pH in a stream receiving acid mine drainage.

Water samples were collected at irregular intervals at two sampling sites in the stream--one within the study zone and one approximately 5 m upstream. A limited number of water samples (2-8) were collected from each of the four wells. Water samples were filtered upon collection through 0.1 micrometer membranes. Within the scope of this reconnaissance study, all four wells are considered to be adjacent to the one stream sampling site within the study zone. In the discussion of results, time is given as elapsed time from the start (hour 0) of the sodium addition and pH adjustment. The variation of pH in the wells was minimal in well A (pH 3.7), well C (pH 3.8) and well D (pH 4.7). In well B, pH the range of observed pH was 3.3 to 4.2.

RESPONSE TO LITHIUM INJECTION

Lithium concentrations had reached plateau values prior to the day of the reconnaissance sampling. Table 1 contains lithium concentrations at hour 3. Background concentrations of lithium in the stream and in the wells were on the order of several hundreths of a milligram per liter. Lithium concentrations in the stream had reached 0.5 mg/L (milligrams per leter) (approximately); thus, lithium concentrations in the wells are an indication of the extent of water contribution from the stream to the substream zone.

Table 1. Lithium concentration at hour 3

[mg/L, milligrams per liter]

Sampling site	Concentration (mg/L)
Stream above study zone	0.54
Stream in study zone	.53
Well A	.52
Well B	.46
Well C	.36
Well D	.04

Relative to the stream concentrations, lithium concentrations in wells A and B were sufficiently great to conclude that (1) water from the stream definitely is entering the substream zone, and (2) the contribution of streamwater is significant, in this zone, tens of centimeters from the stream edge. On the basis of the lithium data alone, water in well A could not be distinguished from streamwater. Lithium concentrations in well C were indicative of a mixture of stream and subsurface water, whereas little, if any, streamwater had entered well D.

RESPONSE TO SODIUM INJECTION

Steady, plateau concentrations for lithium clearly indicate interaction of the substream zone with instream water. The sharp changes in sodium concentrations in the streamwater caused by the successive additions can give indications of the temporal responsiveness of the substream zone to concentration changes in the stream. Table 2 contains the maximum sodium concentrations during each of three periods (during additions 1 and 2, and after the additions). Comparing the instream concentrations within the study zone to concentrations in each of the wells shows a wide range in the responsiveness within the subtream zone. In well B, the first response to sharp changes of instream sodium was virtually concurrent with the instream change. In wells A and C, response was delayed, as indicated by concentrations that only began to increase during the first addition. In well D, sodium concentration did not increase during the first 6 hours.

Table 2. Maximum sodium concentrations

[mg/L, milligrams per liter; -, no data]

Sampling site	Concentration (mg/L)		
	Addition 1 hours 0-3	Addition 2 hours 3-6	Postadditions hours 6-9
Stream above study zone	2.7	2.8	2.7
Stream in study zone	17.6	30.5	4.8
Well A	2.8	5.4	14.7
Well B	17.5	19.0	8.5
Well C	3.6	6.0	8.0
Well D	2.5	2.6	-

RESPONSE TO pH ADJUSTMENT

Table 3 lists the range of copper concentrations observed in three time periods: preresponse, response, and postresponse. Ambient instream copper concentrations ranged from 0.17 to 0.20 mg/L. A response in the stream to the adjusted high pH was a decrease in copper concentration. Between hours 3 and 6, copper concentration at the stream site within the study zone ranged from 0.12 to 0.16 mg/L. During 9 hours of sampling within the substream zone, copper concentrations differed most clearly between sites. Concentrations in wells A and D relative to concentrations in the stream were always high and low, respectively. In wells B and C, concentrations did not differ from ambient concentrations in the stream in the preresponse and response periods, and were lowest in the postresponse period. Given the ranges of the limited preresponse data, this difference may be within the range of ambient variation.

Table 3. Range of copper concentrations

[mg/L, milligrams per liter; precision of analysis was +/- 0.016 mg/L; -, no data; single samples listed in "Low" column]

Sampling site	Concentration (mg/L)					
	Preresponse[1] hours 0-3[2]		Response hours 3-6		Postresponse hours 6-9	
	Low	High	Low	High	Low	High
Stream above study zone	0.18	0.19	0.18	0.20	0.17	0.18
Stream in study zone	.17	.20	.12	.16	.18	.20
Well A	.20	-	.21	-	.19	-
Well B	.16	.20	.18	-	.16	.17
Well C	.17	.18	.17	.19	.16	.16
Well D	.03	-	.03	-	-	-

[1] During the first pH adjustment (hours 0 - 3), copper concentration in the stream did not exhibit a readily identified response. During the second pH adjustment (hours 3-6), when pH exceeded 5.5, the response was unambiguous.

[2] A brief, 10 to 15 minute time span of transient concentrations was excluded from characterizing the beginning of each period. Such transient concentrations result from processes acting on time scales shorter than those relevant to transport through the substream zone.

The solely hydrologic interactions observed with the lithium and sodium transport into the substream have been obscured for dissolved copper. The chemical mechanisms affecting copper concentration in the substream zone were not investigated in this study. However, the reconnaissance does suggest that chemical processes are active along with the hydrologic interaction.

DISCUSSION

A reconnaissance study was conducted to identify interaction of the substream zone with instream transport. This study was an adjunct to an experimental study of trace-metal retention associated with the streambed. The variation within the substream of these hydrologic and chemical interactions is summarized in table 4. The steady maintenance of lithium concentration showed that the stream and the substream zone do exchange water, at least on a time scale of days. As the pulse of sodium in the stream passed through the study zone, the response within the substream ranged among the well sites from virtually concurrent arrival, to a delay of hours, to no response (indicating short-term hydrologic isolation from the channel). For dissolved copper, a concentration change was evident in wells B and C, but, in this reconnaissance study, the ambient differences between sites in the substream were more definitive than any observed experimentally induced change.

Table 4. Reconnaissance of interactions with the substream zone

Sampling site	Steady increase of lithium	Sharp increase of sodium	Variation of copper
	Significant water contributions	Responsiveness	Comparison to ambient stream
Well A	Stream	Delayed	Remains high
Well B	Stream	Concurrent	Similar range
Well C	Mixture	Delayed	Similar range
Well D	Subsurface	No Response	Remains low

In acidic, mountain streams, watershed and instream processes are integrated over wide ranges of temporal and spatial scales to control instream chemistry (McKnight and Bencala, 1990). Specifically in St. Kevin Gulch, there is a definite, highly variable, hydraulic connection between the substream zone and the stream channel. Chemical reactions within the substream may moderate the magnitude of variations in concentration of solutes transported from the stream to substream zones. Thus, the coupled hydro-chemical interaction of the substream zone with instream solute transport may differ among solutes.

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PREDICTIVE MODELING OF COPPER, CADMIUM, AND ZINC PARTITIONING BETWEEN STREAMWATER AND BED SEDIMENT FROM A STREAM RECEIVING ACID MINE DRAINAGE, ST. KEVIN GULCH, COLORADO

By Kathleen S. Smith[1,2], James F. Ranville[1,2], and Donald L. Macalady[2]

ABSTRACT

St. Kevin Gulch is a small mountain stream that receives acid mine drainage from an abandoned mining area. The streamwater carries elevated concentrations of iron, aluminum, copper, cadmium, zinc, and several other elements. The streambed is coated with abundant iron-rich hydrous oxides. This work examines pH-dependent partitioning of copper, cadmium, and zinc between streamwater and bed sediment collected from three sites along St. Kevin Gulch. Observed metal-partitioning behavior is compared with computer-model simulations using a surface-complexation sorption model and the assumption that hydrous iron oxide is the sole sorbent material for metals. Results show that the sorption model is able to predict copper and zinc partitioning, but slightly underestimates cadmium partitioning to the sediment. Partitioning behavior of copper and zinc appears to be dominated by sorption on hydrous iron oxide present in the bed sediment.

INTRODUCTION

St. Kevin Gulch is a small, subalpine mountain stream near Leadville, Colo. It receives acidic (pH 2.8), metal-rich drainage from an abandoned mine dump-mill tailings area (labeled "Mine Dump" in fig. 1). The gulch enters a wetland before its confluence with Tennessee Creek (fig. 1), a tributary of the Arkansas River. Downstream from the tailings area, the pH of St. Kevin Gulch varies between 3.2 and 4.6. The streamwater contains elevated concentrations of iron (Fe), aluminum (Al), zinc (Zn), copper (Cu), and cadmium (Cd) as well as other elements (table 1). The streambed sediment contains abundant hydrous iron oxides (HIO); at sites just downstream from the tailings inflows, the streambed sediment consists of about 40 weight percent Fe (table 2). The streambed sediment also contains significant amounts of organic carbon and detrital materials (table 2).

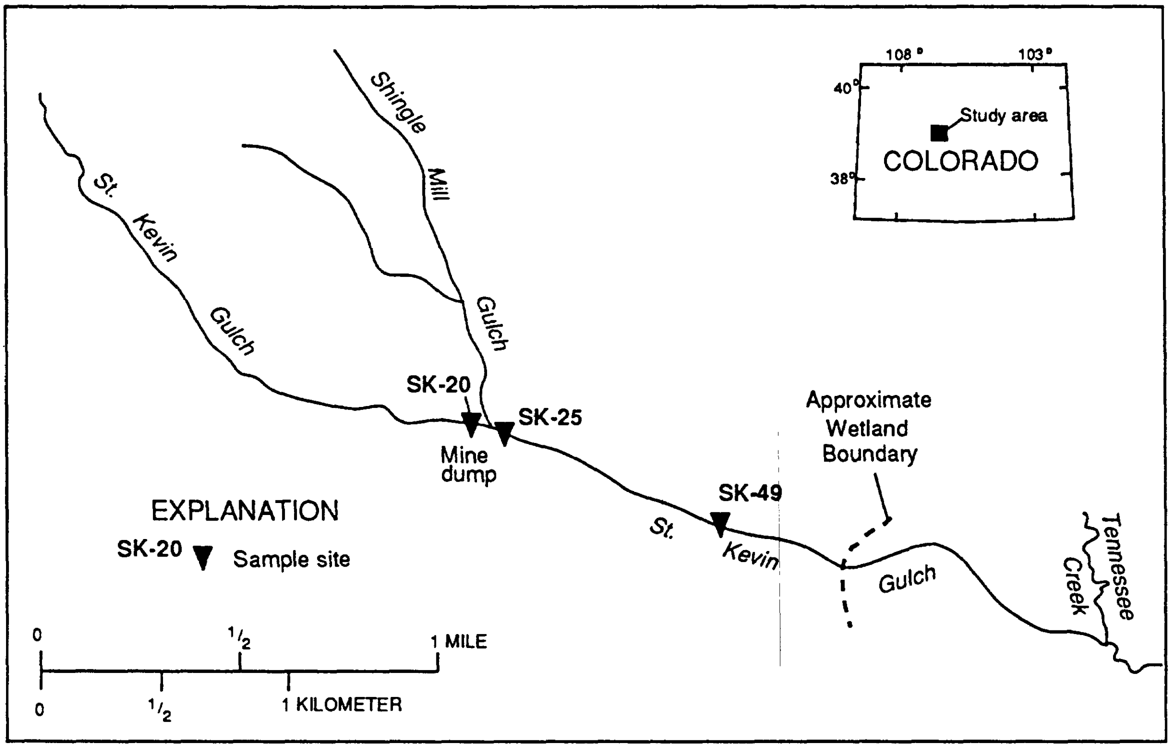

Figure 1. *Sample-collection sites along St. Kevin Gulch (modified from McKnight and others, 1988, fig. 1).*

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[1] U.S. Geological Survey, Denver, Colo.

[2] Department of Chemistry and Geochemistry, Colorado School of Mines, Golden, Colo.

Table 1. *Water chemistry of unfiltered samples from three sites along St. Kevin Gulch on two dates*[1]

[mg/L, milligrams per liter; µg/L, micrograms per liter; mg C/L, milligrams carbon per liter; --, below the limit of detection by inductively coupled plasma-atomic emission spectrometry]

	July 18, 1989			October 6, 1989		
Constituent	SK-20	SK-25	SK-49	SK-20	SK-25	SK-49
Ca (mg/L)	18	11	12	23	18	15
Zn (mg/L)	13	7.4	8.0	16	10	9.5
Si (mg/L)	7.7	6.3	6.5	11	8.9	7.9
Fe (mg/L)	[2]7.5	[2]3.1	[2]1.2	[2]6.0	[2]4.9	[2]1.8
Mn (mg/L)	7.4	3.7	3.6	10	6.4	5.2
Mg (mg/L)	6.7	4.2	4.2	8.4	6.2	5.2
Al (mg/L)	4.1	2.2	2.5	5.3	3.5	3.7
Na (mg/L)	2.8	2.6	2.7	5.2	5.2	4.5
K (mg/L)	.5	.6	.5	.9	.7	.9
Cu (µg/L)	300	160	160	[3]259	[3]155	[3]154
Cd (µg/L)	[4]75	[4]40	[4]45	[3]62.5	[3]38.6	[3]47.1
P (µg/L)	70	100	120	80	170	120
Ni (µg/L)	[4]60	[4]50	[4]50	[3]37.5	[3]24.3	[3]23.6
Sr (µg/L)	40	30	30	60	50	40
Ba (µg/L)	30	30	30	40	40	30
Pb (µg/L)	[4]25	[4]15	[4]25	[3]12.9	[3]9.3	[3]17.7
Co (µg/L)[5]	[4]20	[4]10	[4]10	[3]21.3	[3]13.0	[3]11.9
Ti (µg/L)[5]	--	30	--	40	60	30
SO_4^{2-} (mg/L)[6]	179	75	75	224	134	121
pH (standard)[7]	3.58	3.96	4.03	3.34	3.67	3.72
DOC (mg C/L)[5,8]	.4	.6	.7	.4	.4	.4

[1] Analyses were performed by inductively coupled plasma-atomic emission spectrometry (Lichte and others, 1987) unless otherwise noted.

[2] Analyzed by flame atomic absorption spectrophotometry

[3] Analyzed by inductively coupled plasma-mass spectrometry

[4] Analyzed by flameless atomic absorption spectrophotometry (Perkin- Elmer Corporation, 1977)

[5] Not included in the MINTEQA2 input file

[6] Analyzed by ion chromatography (Fishman and Pyen, 1979)

[7] Field measurement

[8] Analyzed by a high-temperature wet persulfate oxidation technique

Hydrous oxides in sediment are thought to control the aqueous concentrations and affect transport of trace metals in many natural systems (Jenne, 1968; Singh and Subramian, 1984). Examination of water and sediment from St. Kevin Gulch offers the opportunity to investigate the role of HIO in the attenuation of dissolved trace elements from acid mine drainage.

This paper examines the pH-dependent partitioning of Cu, Cd, and Zn between streamwater and bed sediment from St. Kevin Gulch. Computer-simulation results (derived from a surface-complexation sorption model) were compared to experimental data (derived from natural streamwater-bed-sediment experiments). The approach was to obtain streamwater-bed-sediment mixtures from each of three sites along St. Kevin Gulch (fig. 1) at different times of the year, incrementally raise the pH in parts of the mixtures, and analyze filtered samples of the mixtures. Experimental data were then compared with simulations of Cu, Cd, and Zn sorption onto pure-phase, synthetic HIO using the computer program MINTEQA2 (Allison and others, 1991) coupled with the Generalized Two-Layer Sorption Model (Dzombak and Morel, 1990).

CHEMICAL REACTIONS ON METAL-OXIDE SURFACES

Hydrous metal oxides can both bind and release protons resulting in either a net positive or a net negative surface charge. The sign and magnitude of this charge depends on the pH of the surrounding water, the particular metal oxide of interest, the ionic strength, and the presence of specifically-sorbed or complexing cations and(or) anions (Parks and de Bruyn, 1962; Parks, 1990). Generally, hydrous metal oxides carry a net positive surface charge in very acidic waters and a net negative surface charge in alkaline waters.

Sorption of cations on metal-oxide surfaces is highly pH dependent, increasing as the pH is increased with concomitant release of protons (James and Healy, 1972a; Schindler and others, 1976; Stumm and others, 1976). Sorption of cations usually occurs over a narrow pH range (typically 1 or 2 pH units) termed the "adsorption edge." The location of the adsorption edge depends on the sorbate cation, the sorbent metal oxide, the sorbate-sorbent ratio, and the presence of competing cations and(or) ligands (Dzombak and Morel, 1987; Davis and Kent, 1990).

Surface-complexation sorption models consider the interaction of ions with metal-oxide surfaces to be coordination reactions that involve specific interactions between the ions and surface functional groups (Davis and Kent, 1990). The Generalized Two-Layer Sorption Model (Dzombak and Morel, 1990) used in this study treats the oxide-solution interface as a single surface layer (where specific sorption reactions take place) and a Gouy-Chapman diffuse layer (where counterions are located). To simulate cation sorption, the model uses two types of surface-binding sites, termed "strong" (high affinity) and "weak" (low

Table 2. *Chemistry of iron-rich bed sediment from three sites along St. Kevin Gulch on two dates*[1]

[wt. %, weight percent; >, greater than the given upper limit; ppm, parts per million; --, below the limit of detection by inductively coupled plasma-atomic emission spectrometry]

Constituent	July 18, 1989 SK-20	July 18, 1989 SK-25	July 18, 1989 SK-49	October 6, 1989 SK-20	October 6, 1989 SK-25	October 6, 1989 SK-49
Fe (wt.%)	38.4	40.7	23.5	42.9	41.2	16.1
C (wt.%)[2]	3.7	5.4	8.8	3.2	3.1	8.5
S (wt.%)[3]	3.1	2.5	1.1	3.3	3.6	.60
Al (wt.%)	.67	.51	4.5	.61	.30	5.0
Si (wt.%)[4]	.5	.3	2	2	.7	>10
P (wt.%)	.31	.27	.30	.35	.21	.20
K (wt.%)	.23	.11	1.4	.20	.09	1.9
Mg (wt.%)	.05	.03	.30	.04	.02	.32
Na (wt.%)	.04	.03	.33	.04	.15	.52
Ca (wt.%)	.03	.03	.22	.02	.01	.21
Ti (wt.%)	.02	.01	.10	.02	.01	.14
Zn (ppm)	243	306	2,480	311	167	1180
Pb (ppm)	132	182	560	124	106	558
Th (ppm)	130	149	156	85	141	115
Mn (ppm)	106	97	537	109	132	436
As (ppm)	72	52	59	92	45	40
Cu (ppm)	57	107	201	65	56	130
Ba (ppm)	43	21	224	46	20	326
Cr (ppm)	17	19	47	13	16	43
Ag (ppm)	15	14	63	17	9	61
Ce (ppm)	15	14	100	14	7	90
Nd (ppm)	12	17	64	8	6	49
Sr (ppm)	12	7	68	12	4	125
La (ppm)	10	7	46	6	3	39
Ga (ppm)	7	8	18	11	8	17
Co (ppm)	4	4	7	5	5	6
Mo (ppm)	4	9	8	--	6	4
Cd (ppm)	--	--	16	2	--	6
Li (ppm)	--	--	15	3	--	20
Ni (ppm)	--	--	11	--	--	11
Sc (ppm)	--	--	8	--	--	7
V (ppm)	--	--	30	15	9	34
Y (ppm)	--	--	19	2	2	14

[1] Analyses were performed by inductively coupled plasma-atomic emission spectrometry (Lichte and others, 1987) unless otherwise noted. Sediment was digested in a mixture of nitric, hydrochloric, perchloric, and hydrofluoric acids

[2] Analyzed by a combustion-coulometric technique (Lee and Macalady, 1989). Total carbon results represent organic carbon due to low pH in St. Kevin Gulch streamwater

[3] Analyzed by a combustion-infrared technique (Jackson and others, 1987)

[4] Analyzed by semiquantitative emission spectrography (Grimes and Marranzino, 1968)

affinity) sites. Dzombak and Morel (1990) have compiled an internally-consistent data base of intrinsic constants for cation and anion sorption on HIO. The data base was developed using fixed values for both surface site densities and specific surface area (table 3). An optimization program was used to fit surface-complexation constants for selected literature sorption data. These selected data were obtained from laboratory studies of single-solute synthetic HIO (pure HIO phase) systems.

METHODS

Sample Collection and Preparation

Streamwater-streambed material was collected from St. Kevin Gulch, sites SK-20, SK-25, and SK-49 (fig. 1), on July 18 and October 6, 1989. The samples were collected by placing HIO-coated streambed rocks and pebbles into a

Table 3. *Summary of hydrous iron oxide properties and intrinsic adsorption constants used for modeling experimental data with MINTEQA2 + Generalized Two-Layer Sorption Model*

Molecular weight = 89 g Fe/mole (assuming $Fe_2O_3 \cdot H_2O$)
Specific surface area = 600 m^2/g
High-enery site density = .005 moles/mole Fe
Low-energy site density = .2 moles/mole Fe

Surface complexation constants:[1]

Strong copper binding	log(K)	=	2.85
Weak cooper binding	log(K)	=	.60
Strong zinc binding	log(K)	=	.97
Weak zinc binding	log(K)	=	-1.99
Strong cadmium binding	log (K)	=	.43
Weak cadmium binding	log(K)	=	-2.90

[1] Reactions of the cationic metals (M^{2+}) with the hydrous iron oxide surface (=Fe) are:

$$=FeOH^{o} + M^{2+} = =FeOM^{+} + H^{+}$$

plastic bottle containing streamwater from that site. The bottle was shaken, placing the HIO coatings in suspension. The streamwater-streambed slurry was then decanted into a polyethylene bottle. This procedure was repeated several times to obtain a composite sample from each site. Unfiltered streamwater was collected concurrently at all sites. Both unfiltered and filtered (0.1-µm (micrometer)) streamwater samples were collected for chemical analysis. The pH, temperature, and conductivity of the streamwater was measured in the field at the time of sample collection.

A part of each of the streamwater-streambed slurries was allowed to settle overnight, decanted, and air-dried at room temperature. These dried streambed materials were stored for chemical analysis. Parts of each of the filtered streamwater samples were refrigerated and stored for sulfate analysis. Subsamples of each of the unfiltered and filtered streamwater were acidified with concentrated nitric acid and stored for chemical analysis. The remainder of the streamwater-streambed slurries were adjusted to the same weight of solid material per volume (2.9 grams per liter) for each sample by addition of unfiltered streamwater collected concurrently with the streamwater streambed slurries. These normalized mixtures were used for the pH-dependent metal-partitioning experiments.

Metal-Partitioning Experiments

Metal-partitioning experiments were performed with the six streamwater-streambed mixtures over a pH range of ambient pH to pH>6. An initial potentiometric acid-base titration was performed on a part of each mixture to determine the amount of sodium hydroxide (NaOH) necessary to bring the pH of the mixture to pH>6. The pH was adjusted (by addition of various volumes of 0.2 moles/liter NaOH) in a series of bottles containing 40 milliliters of each of the mixtures. No other substances were added. The bottles were allowed to sit for approximately 6 hours at room temperature with occasional shaking. Six hours was deemed to be adequate based on previous sorption experiments (Smith and others, 1989). After the 6-hour period, part of the mixtures was separated by filtration through 0.1-µm nitrocellulose filters. The filtrates were stored for chemical analysis and final pH was measured in the remaining mixtures. Determination of the solute concentrations at a known pH was used as a measure of pH-dependent metal-partitioning reactions. Blank experiments were carried out in unfiltered streamwater adjusted to pH values ranging from ambient to pH 6 to differentiate sorption reactions from solubility reactions.

Sample Analysis

All samples were analyzed in random sequence to convert any systematic analytical errors to random errors. The results are given in tables 1 and 2. Electrophoretic mobility measurements (Hunter, 1981) were made on suspensions of bed sediment in streamwater to determine the surface charge of the sediment. An electrophoretic light-scattering technique (Ranville and others, 1991, this Proceedings) was used for these measurements.

Modeling Approach

Sorption of Cu, Cd, and Zn on HIO was modeled using the Generalized Two-Layer Sorption Model and data base of surface-complexation constants of Dzombak and Morel (1990). The same HIO properties were used in this study as were used by Dzombak and Morel to fit the surface-complexation constants (table 3). Only two solid phases, ferrihydrite and amorphous aluminum hydroxide, were allowed to precipitate in the model simulation because they were considered to be the most likely solids to precipitate during the time frame (6 hours) of the metal-partitioning experiments. Other trace-metal hydroxide phases did not exceed saturation in the computer simulations. Water chemistry (table 1) at each site was input to the computer program MINTEQA2 (Allison and others, in press) coupled with the Generalized Two-Layer Sorption Model (Dzombak and Morel, 1990). This program computes sorption reactions and solution equilibria simultaneously in a self-consistent manner. The weight percent Fe in the sediment (table 2) was assumed to represent amorphous iron oxide and calculations of binding-site concentrations and total amorphous Fe were based on this assumption.

RESULTS AND DISCUSSION

Figure 2 shows computer-model predictions and experimental data for the three sampling sites on July 18 and October 6, 1989. Variation between model predictions for different sites and dates is primarily due to the amount of iron present in the sediment.

Agreement between model sorption predictions and experimental partitioning data for Cu and Zn in the July experiments is excellent. Agreement for Cu and Zn in the October experiments is good, although the predictions slightly underestimate partitioning of Cu and Zn to the sediment. This underestimation is especially conspicuous for site SK-49, where the least amount of iron and the greatest amount of carbon is present in the sediment (table 2). These results indicate that Cu and Zn partitioning is dominated by sorption on HIO in the sediment. There does not appear to be a large seasonal variation in metal partitioning trends.

Cadmium partitioning to the sediment is underestimated in both sets of data. Benjamin and Leckie (1982) showed that model predictions underestimate Cd sorption on HIO in the presence of sulfate. One possible explanation for this enhanced Cd sorption is binding of Cd sulfato complexes to HIO (Benjamin and Leckie, 1982). Anderson and Benjamin (1985) reported enhanced Cd sorption on HIO with incorporated silicon (Si) relative to pure HIO, but they observed no effect on Cu and Zn sorption. Our results are consistent with their observations. In addition, Si concentrations in filtrates from our metal-partitioning studies decreased with increasing pH, further indication of incorporation of Si into the HIO.

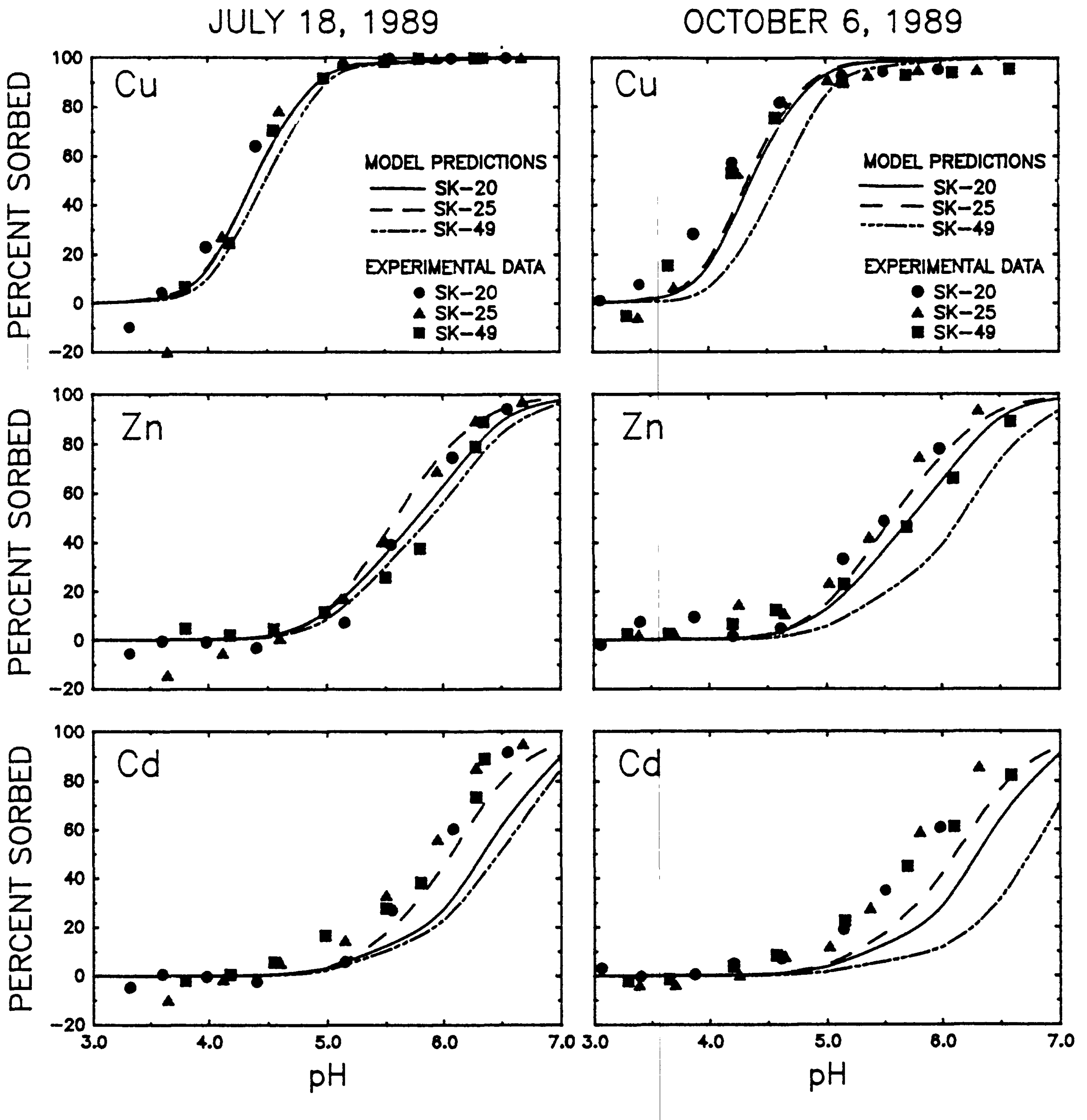

Figure 2. *Computer-model sorption predictions (curves) and experimental partitioning data (symbols) for three sites along St. Kevin Gulch on July 18 and October 6, 1989.*

Figure 3 illustrates the variation in electrophoretic mobility of the streambed sediment with pH for the July metal-partitioning experiments. It is clear that the electrical character and surface charge of the sediment from site SK-49 is different than that from sites SK-20 and SK-25, yet there is no significant difference between the simulation-versus-experimental agreement for Cu and Zn at the three sites in July (fig. 2). Possible explanations for the more negative surface charge at site SK-49 include one or more of the following: (1) increased presence of detrital minerals (for example, clay minerals), (2) decreased amounts of positively charged surface complexes (James and Healy, 1972b; Schindler, 1981), (3) increased amounts of negatively charged surface complexes, and (4) the presence of sorbed or coprecipitated organic matter or biotic materials. Several researchers have shown that sorbed natural organic matter can have a strong effect on surface properties (Hunter and Liss, 1979; Tipping and Cooke, 1982; Ranville and others, 1991, this Proceedings) and metal sorption (Davis, 1982; Tipping and others, 1983), and humic substances are known to bind to metal oxides (Tipping, 1981; Davis, 1982).

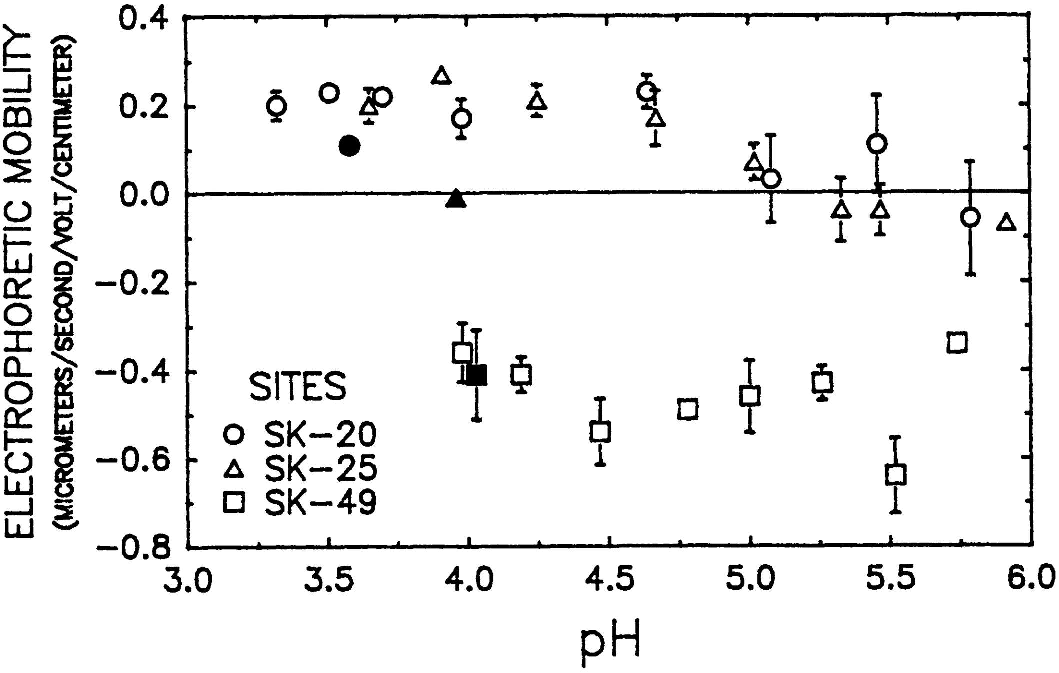

Figure 3. *Electrophoretic mobilities of St. Kevin Gulch sediment as a function of pH. Open symbols represent pH-adjusted mixtures from the July 18, 1989, metal-partitioning experiments and filled symbols represent field samples collected on July 18, 1989. Error bars represent the standard deviation of triplicate measurements.*

The streambed sediment contains a substantial amount of organic carbon (table 2). It is noteworthy that this carbon does not appear to have enough of an effect on Cu and Zn partitioning to cause the experimental data to deviate significantly from pure-phase HIO sorption-model predictions (Schindler and Stumm, 1987). The partitioning of a metal cation in systems containing different sorbents depends on the binding intensity (surface-complexation constant), binding capacity (surface site density), and abundance (concentration) of each sorbent. In the case of St. Kevin Gulch, it appears that HIO is abundant enough to dominate metal-partitioning reactions. In addition, Cu- and Zn-binding intensities and binding capacities are large for HIO surfaces. It is also possible that other elements (for example, Fe and Al) are preferentially binding to and tying up the organic functional groups present in the sediment.

ACKNOWLEDGMENTS

We thank N. Loux of the U.S. Environmental Protection Agency for his help with the modeling aspect of this work. Analyses for this study were done in the U.S. Geological Survey Analytical Laboratories of the Branch of Geochemistry, Denver, Colorado. The ICP-AES analyses were performed by P. Briggs, D. Fey, and M. Malcolm, and ICP-MS analyses were performed by A. Meier and G. Riddle. Emission spectrography analysis of Si in sediment was done by S. Sutley. The authors would like to acknowledge K. Cabral, J. Curry, W. Ficklin, L. Jackson, J. McHugh, C. Papp, and W. Sadler for their help with analytical work, and M. Simmons and R. Walker for their help with illustrations. The leadership of B. Kimball, and the help, advice, and support of the Upper Arkansas Project team is greatly appreciated.

SUMMARY

The Generalized Two-Layer Sorption Model was used to successfully predict pH-dependent metal partitioning between streamwater and bed sediment collected from St. Kevin Gulch, a Colorado stream that receives acid-mine drainage. Model predictions were based on pure-phase (hydrous iron oxide) single-sorbent studies. The abundance of hydrous iron oxide in the sediment appears to dominate partitioning of Cu, Cd, and Zn by sorption processes. Partitioning of Cd may also be affected by other processes. In these kinds of iron-dominated systems, the use of a sorption model is beneficial because it can predict metal partitioning with changing pH, sorbent concentration, and streamwater chemistry conditions. Use of the Generalized Two-Layer Sorption Model and accompanying data base does not require extensive characterization of the hydrous iron oxide sorbent. Necessary input to the model includes streamwater chemistry, the amount of amorphous Fe present in the sediment, and calculation of corresponding binding-site concentrations.

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PHOSPHATE UPTAKE BY ALGAE IN A STREAM CONTAMINATED BY ACID MINE DRAINAGE, ST. KEVIN GULCH, LEADVILLE, COLORADO

By Cathy M. Tate[1], Diane M. McKnight[2], and Sarah A. Spaulding[3]

ABSTRACT

Low concentrations of phosphorus (P) in Rocky Mountain streams potentially limit algal growth. Factors altering P concentration, such as adsorption of P onto hydrous iron oxides in streams contaminated by acid mine drainage, can have an important effect on stream biota. An hour-long injection of phosphate ($^{32}PO_4$) containing radioactive phosphorus (^{32}P) into a 175-meter reach of St. Kevin Gulch was used to study pathways by which benthic algae assimilate P for growth in streams contaminated by acid mine drainage. Algae covered 47 percent and hydrous iron oxides 30 percent of the stream channel during the study. Samples of water, suspended solids, algae and hydrous iron oxides were collected at five sites (the three upstream sites were shaded and the two downstream sites exposed to sunlight) to follow the pathways of ^{32}P. ^{32}P in samples of water and algae decreased downstream from the injection site, whereas ^{32}P in samples of hydrous iron oxides indicated no consistent downstream pattern. ^{32}P per milligram dry weight of suspended solids increased greater than twofold in nonshaded compared with shaded sections of the stream channel, which indicates that light altered concentrations of ^{32}P in suspended solids. ^{32}P was greater in algae and adenosine triphosphate extracts of algae than in hydrous iron oxides which indicates algal uptake of ^{32}P directly from water. Prior to the injection, acid phosphatase activity was measured and was greater during the day than at night, which indicates that algae have a greater demand for P during periods of photosynthesis. ^{32}P per streambed area for algae and hydrous iron oxides, indicated that both are important sinks for $^{32}PO_4$ in St. Kevin Gulch. Algae can directly remove and assimilate available phosphate from the water for growth and successfully compete with abiotic pathways (adsorption of phosphates onto hydrous iron oxide) for this limiting nutrient.

INTRODUCTION

Nutrients regulate many ecological processes in stream ecosystems (Meyer and others, 1988). Low concentrations of phosphate measured in many undisturbed stream ecosystems limit algal growth (Tate, 1990). Concentrations of phosphate in Halfmoon Creek, a U.S. Geological Survey Hydrologic Benchmark station in the upper Arkansas River basin in Colorado, typically are below detection limit <10 micrograms per liter (U.S. Geological Survey, 1987, p. 154). At such low concentrations, phosphorus (P) is potentially the limiting nutrient for algal growth in Rocky Mountain streams. Therefore, factors altering P concentrations and transport can have an important effect on stream biota.

Many streams in the Rocky Mountains are affected by acid mine drainage (Moran and Wentz, 1974). St. Kevin Gulch, a tributary of Tennessee Creek about 7 kilometers northwest of Leadville, Colo., is contaminated by acid mine drainage from tailings and abandoned mines (McKnight and others, 1988). Effects of acid mine drainage on stream ecosystems include high concentrations of metals (iron, manganese, aluminum, lead, cadmium, copper, zinc), low pH, and coating of the streambed by hydrous iron oxides (McKnight and others, 1988). These effects can alter P dynamics in stream ecosystems. The chemical nature of stream sediments (the aluminum, iron, and organic content) and low pH in streamwater increase sorption of P by stream sediments (Syers and others, 1973; Meyer, 1979). Precipitation of inorganic phosphate by iron commonly is reported in aquatic ecosystems (Stumm and Morgan, 1981). All these factors can decrease availability of P to stream biota.

Phosphate adsorbs to iron complexes under aerobic, acidic conditions primarily when the iron species is in the oxidized ferric (Fe^{3+}) state (Koenings and Hooper, 1976). Phosphate sorbed to Fe^{3+}-complexes associated with humic material can be released by ultraviolet-induced photoreduction of Fe^{3+} to the ferrous (Fe^{2+}) state (Franko and Heath, 1982). Photoreduction of Fe^{3+} and a corresponding increase in dissolved Fe^{2+} during daylight has been reported for St. Kevin Gulch (McKnight and others, 1988). Thus, photoreduction of Fe^{3+} to Fe^{2+} can release adsorbed phosphate and increase P availability to algae during the day.

Algae produce alkaline and acid phosphatases in response to low concentrations of phosphate (potential P limitation) (Jansson and others, 1988). Phosphatases are enzymes that cleave orthophosphate from organic phosphorus compounds. Thus, increases in acid phosphatase activity of algae possibly indicate P limitation in aquatic ecosystems.

Despite high concentrations of metals and low pH in St. Kevin Gulch, the filamentous green algae, *Ulothrix* sp., occurs in abundance during low flows in August (McKnight, 1988). During this time, P would be expected to be bound chemically to the hydrous iron oxides on the streambed and not to be readily available to the algae. To determine the pathways by which the algae assimilate P for growth in St. Kevin Gulch, the radioactive tracer, $^{32}PO_4$, was injected into the stream channel during August when algae were abundant. $^{32}PO_4$ traces the movement of P at mass levels that do not grossly affect concentrations of this nutrient in the stream channel. This paper reports preliminary results from this onsite experiment.

METHODS

A $^{32}PO_4$ injection was done in a 175-m (meter) reach of St. Kevin Gulch. Sampling stations were located at 13 m (Bio 1), 25 m (Bio 2), 62 m (Bio 3), 116 m (Bio 4) and 175 m (Bio 5) downstream from the injection site (fig. 1). Sites Bio 1 to Bio 3 were shaded by riparian vegetation; sites Bio 4 and Bio 5 were exposed to full sunlight.

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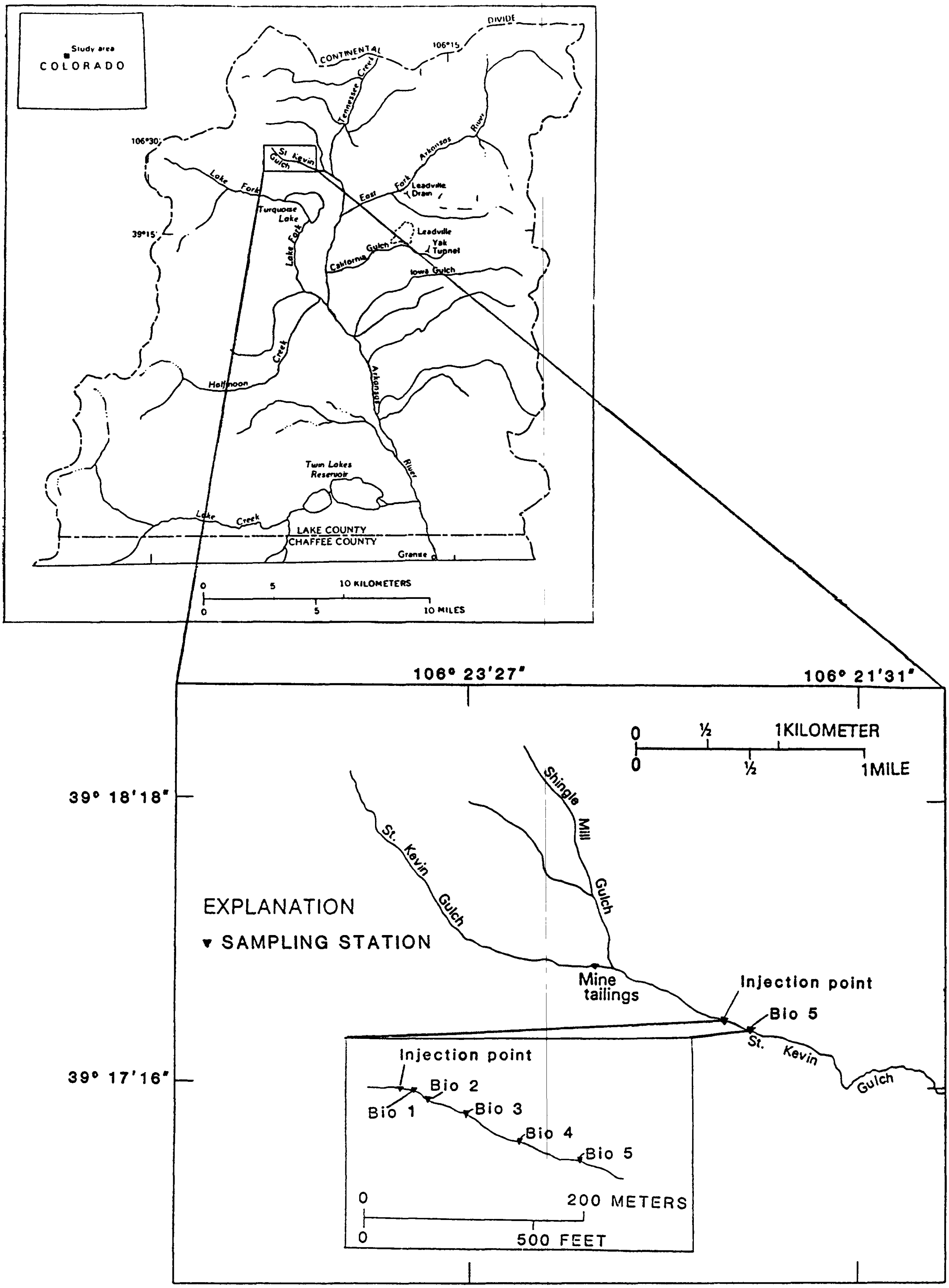
Study area
COLORADO
CONTINENTAL
DIVIDE
106°15
106°30
39°15
Tennessee Creek
Arkansas River
St Kevin Gulch
Lake Fork
East Fork
Leadville Drain
Turquoise Lake
Lake Fork
Leadville
Yak Tunnel
California Gulch
Iowa Gulch
Creek
Halfmoon
Arkansas
Twin Lakes Reservoir
River
Lake Creek
LAKE COUNTY
CHAFFEE COUNTY
Granite
0
5
10 KILOMETERS
0
5
10 MILES
106° 23'27"
106° 21'31"
39° 18'18"
39° 17'16"
0
½
1KILOMETER
0
½
1MILE
Shingle Mill Gulch
St. Kevin Gulch
EXPLANATION
▾ SAMPLING STATION
Mine tailings
Injection point
Bio 5
St. Kevin Gulch
Injection point
Bio 1
Bio 2
Bio 3
Bio 4
Bio 5
0
200 METERS
0
500 FEET

Figure 1. Location of St. Kevin Gulch in the upper Arkansas River basin and sampling sites. (Top figure modified from Kimball and Wetherbee, 1989, fig. B-4; bottom figure modified from Smith and others, 1989, fig. B-24.

Prior to the $^{32}PO_4$ injection, dry weight of algae, hydrous iron oxides and suspended solids, and acid phosphatase activity (APA) of algae, were measured at sites Bio 1 to Bio 4. Site Bio 5 was initially selected to monitor the disappearance of ^{32}P from the water rather than a site of intensive study; therefore, these measurements were not taken at this site.

Percent cover of algae and hydrous iron oxides was measured from the injection point to Bio 5 using a line-transect method (Smith, 1974). Transects were measured at 5-m intervals, and the presence of algae, hydrous iron oxides, mixture of algae and hydrous iron oxides, rocks, wood, and silt were recorded to the nearest 0.05 m across the channel. Percent cover was calculated as the sum of the length in a category divided by the sum of total length measured and then multiplied by 100 percent.

The dry weight of suspended solids was measured by filtering 1 liter of water onto preweighed glass fiber filters (Whatman[4] GF/C, 1.2-micrometer pore size), drying filters at 80 °C (degrees Celsius) and reweighing. The dry weight of algae and hydrous iron oxides in the stream channel was measured from two benthic cores, 2.54 cm^2 (square centimeters) each, of algae and hydrous iron oxides taken *in situ* to a depth of 3 to 5 millimeters. Cores were filtered onto preweighed glass fiber filters, dried at 80 °C, and reweighed.

A core (2.54 cm^2) of algae was taken *in situ* at sites Bio 1 to Bio 4 during the day (1700-1730 hours) and during the night (0400-0430 hours) to estimate APA of algae. APA determinations followed the methods of Boavida and Heath (1984). Phosphatase activity was measured as the rate of hydrolysis of p-nitrophenylphosphate substrate; the release of p-nitrophenol was determined spectrophotometrically as the increase in absorbance at 395 nanometers for a 4-hour period.

The $^{32}PO_4$ injection took place on August 24, 1990. A solution containing 45.4 millicuries of ^{32}P as carrier-free orthophoshoric acid ($H_3{}^{32}PO_4$) and 0.337 g (gram) of P as potassium phosphate (K_2HPO_4) was released into St. Kevin Gulch from 1033 to 1137 hours. Samples of water and suspended solids were collected at the five stations described previously at 3- to 10-minute intervals for 3 hours during and immediately following the injection.

Samples of streamwater were collected using an Antlia pump as a syringe, recording the volume, filtering immediately through a 0.1-micrometer filter and placing a 5-mL (milliliter) subsample of the filtrate into a scintillation vial with 10 mL of scintillation cocktail. The filter was removed and placed in a scintillation vial, and 10 mL of scintillation cocktail was added. Water and filters were counted for ^{32}P on a Beckman LS 7800 Liquid Scintillation Counter.

Two samples of algae and one sample of hydrous iron oxides were collected at 0.5, 1, 4, 8, 12, 18, and 24 hours after the injection began at sites Bio 1 to Bio 4 and at 4 and 24 hours at site Bio 5. One algal sample was collected for ^{32}P counts and the second for adenosine triphosphate (ATP) extraction. An additional sample of hydrous iron oxides was collected at 24 hours for ATP extraction. Algae were collected by forceps from riffle areas; hydrous iron oxides were collected by aspirating sediments from the stream bottom.

Samples of algae and hydrous iron oxides were filtered onto preweighed glass fiber filters, placed on planchets, and counted for ^{32}P on a LB 5100/5110 Tennelec Low Background Proportional Counter. After counting, samples were dried at 80 °C and reweighed for determination of dry weight.

ATP was extracted from algae to determine if the added ^{32}P was assimilated into the algal cell. ATP is the energy source for biochemical reactions inside cells and P is used in synthesis of ATP. ATP extraction of samples of algae and hydrous iron-oxides filtered onto glass fiber filters followed the procedure of Karl and Holm-Hansen (1978). A 1-mL subsample of the ATP extract was pipetted into a scintillation vial with 10 mL of scintillation cocktail and counted for ^{32}P, as described previously for water samples. The remainder of the sample was frozen for later ATP analyses.

All samples for ^{32}P were counted within 4 days after collection, and counts were corrected to the same time for radioactive decay.

RESULTS AND DISCUSSION

Mean APA for a 2.54-cm^2 core of algae was greater during the day (8.24×10^{-2} µM/min (micromoles per minute)) than during the night (3.24×10^{-2} µM/min).

Concentrations of ^{32}P in water decreased downstream from the injection point, whereas concentrations of ^{32}P in suspended solids indicated no consistent downstream pattern (table 1). Concentrations of suspended solids were greater in upstream sites (table 1, Bio 1 and Bio 2) compared to downstream sites (table 1, Bio 3 and Bio 4). The quantity of ^{32}P per mass of suspended solids at the lighted site (Bio 4) increased greater than twofold relative to upstream values (table 1).

Table 1. *Mean radioactive phosphorus (^{32}P) counts in the water component during the phosphate ($^{32}PO_4$) injection into St. Kevin Gulch*

[No., number; ^{32}P, phosphorus 32; dpm/mL, disintegrations per minute per milliliter; mg DW/L, milligram dry weight per liter; dpm/mg DW, disintegrations per minute per milligram dry weight; dashes indicate not sampled]

Sampling site identification (fig. 1)	Counts in water component[1]				
	Sample size (No.)	Concentration of ^{32}P in water (dpm/mL)	Concentration of ^{32}P in suspended solids (dpm/mL)	Concentration of suspended solids[2] (mg DW/L)	Concentration of ^{32}P in suspended solids[3] (dpm/mg DW)
Bio 1	19	2,629	138	0.82	160,000
Bio 2	13	1,885	204	.90	230,000
Bio 3	17	1,194	87	.50	190,000
Bio 4	13	716	315	.53	600,000
Bio 5	9	234	179	--	--

[1] Means includes only samples that had concentrations of ^{32}P greater than background.

[2] Values represent sample size of 1.

[3] Values calculated by multiplying the mean concentrations of ^{32}P in suspended solids by 1,000 milliliters per liter divided by the concentrations of suspended solids.

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[4] Use of brand, firm, or trade names in this paper is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

^{32}P in benthic algae decreased downstream, whereas ^{32}P in hydrous iron oxides indicated no pattern and on a dry weight basis was lower than the quantity measured in algae (table 2). ^{32}P in the ATP extract from algae (table 2) was greater than the ATP extracts from hydrous iron oxides, which averaged 189 disintegrations per minute per milliliter. The ratio between ^{32}P in algae and water (table 2) was relatively constant in the two lighted sites but was variable in shaded sections. The dry weight of algae per area increased downstream (table 2); however, this downstream increase may be due not to greater algal biomass but to a greater proportion of the sample containing iron oxides. An increase in the coating of algae by hydrous iron oxides was observed at the downstream sites. In contrast, the dry weight of hydrous iron oxides per area indicated no consistent pattern (table 2).

Table 2. *Mean radioactive phosphorus (^{32}P) counts and quantities of algae and hydrous iron oxides during the phosphate ($^{32}PO_4$) injection into St. Kevin Gulch*

[^{32}P, phosphorus 32; dpm/mg DW, disintegrations per minute per milligram dry weight; dpm/mL, disintegrations per minute per millilter; ATP, adenosine triphosphate; mg DW/cm^2, milligrams dry weight per square centimeter; dashes indicate not sampled]

Sampling site identification (fig. 1)	^{32}P in algae[2] (dpm/mg DW)	^{32}P in hydrous iron[2] oxides (dpm/mg DW)	Dpm/mg DW in algae dpm/mL in water[4]	^{32}P in ATP extract of algae[3] (dpm/mL)	Algae (mg DW/ cm^2)	Hydrous iron oxides (mg DW/ cm^2)
Bio 1	42,800	1,090	17.1	2,929	6.5	391
Bio 2	22,500	3,090	12.0	2,978	38.4	874
Bio 3	16,200	3,350	13.5	1,983	47.0	214
Bio 4	15,100	1,170	21.1	759	86.7	524
Bio 5	4,500	1,080	21.2	--	--	--

[1] Values are the mean of two samples.

[2] Values are the mean of seven samples for sites Bio 1 to Bio 4 and the mean of two samples for Bio 5.

[3] Values are the mean of nine samples.

[4] Values calculated by dividing ^{32}P in algae (table 2) by ^{32}P in water (table 1).

Algae covered between 22 and 59 percent of the stream channel (table 3). Hydrous iron oxide cover generally decreased downstream (table 3). In the Bio 4 to Bio 5 section, the percentage of algal and hydrous iron oxide cover decreased; however, the mixture of the two became more prevalent (table 3). The proportion of ^{32}P per streambed area was greater in the hydrous iron oxide component compared to the algal component at the two upstream sections (table 3, O m to Bio 2), but the opposite trend was observed at the two downstream sites (table 3, Bio 2 to Bio 4).

The downstream decrease in concentrations of $^{32}PO_4$ in water (table 1) could be attributed to three factors--biotic uptake, abiotic sorption, or dilution by increase in streamflow. Previous tracer studies done in August, measured similar concentrations of Li^+ (no dilution of the tracer) at sites near Bio 3 and Bio 5, which indicates that discharge between these two sites does not increase in a downstream direction (McKnight and others, 1988, p. 637). The appearance of ^{32}P in hydrous iron oxides indicates that abiotic sorption occurred during the injection (table 2). However, the lower concentration of ^{32}P in hydrous iron oxides compared to algae and the lack of a downstream pattern of ^{32}P in hydrous iron oxides (table 2) possibly indicate that sorption was not solely responsible for the downstream decrease in concentrations of ^{32}P measured in streamwater. In contrast, the concentrations of ^{32}P in algae decreased downstream in a similar pattern and the ratio of ^{32}P in algae to the water was relatively constant (table 2). Thus, the downstream decrease in concentrations of ^{32}P in water probably was due to a combination of algal uptake and abiotic sorption.

When water entered the lighted section of the stream channel, there was an increased association of ^{32}P with suspended solids compared to water, as indicated by the ^{32}P

Table 3. *Stream channel area, algal and hydrous iron oxide cover of streambed, and weighted proportion of radioactive phosphorus (^{32}P) in algae and iron oxides in St. Kevin Gulch*

[m^2, square meters; Other, includes rocks, wood, and silt in stream channel; ^{32}P, phosphorus 32; dpm/m^2 x 10^9, disintegrations per minute per square meter times 1,000,000,000; 0 m, injection point; dashes indicate not calculated]

Section of channel	Channel area (m^2)	Algal cover (percent)	Hydrous iron oxide cover (percent)	Algae + hydrous iron-oxide mixture (percent)	Other (percent)	^{32}P in algae in stream channel[1] (dpm/m^2 x 10^9)	^{32}P in hydrous iron oxides in stream channel[2] (dpm/m^2 x 10^9)
0 m-Bio 1	20	22	69	9	0	0.6	2.9
Bio 1-Bio 2	21	57	36	0	7	4.9	9.7
Bio 2-Bio 3	53	59	23	7	11	4.5	1.6
Bio 3-Bio 4	74	51	29	9	11	6.7	1.8
Bio 4-Bio 5	85	37	17	26	19	--	--
0 m-Bio 5	250	47	30	10	13	--	--

[1] Values calculated by multiplying ^{32}P in algae (table 2) by the quantity of algae per area (table 2) multiplied by 10,000 square centimeters per square meter multiplied by percent algal cover (table 3).

[2] Values calculated by multiplying ^{32}P in hydrous iron oxides (table 2) by the quantity of hydrous iron oxides per area (table 2) multiplied by 10,000 square centimeters per square meter multiplied by percent hydrous iron oxide cover (table 3).

per mass of suspended solids (table 1). This result was unexpected. Suspended solids were assumed to be dominated by Fe^{3+} colloids. McKnight and others (1988) have reported that rapid changes in iron speciation (photoreduction of Fe^{3+} to Fe^{2+}) can occur in response to changes in solar radiation in St. Kevin Gulch. Thus, photoreduction of Fe^{3+} to Fe^{2+} in iron complexes in the lighted section of the stream channel was expected to release adsorbed P, not increase P associated with iron colloids. Perhaps the faster turnover of iron, that is the dissolution of Fe^{3+} to Fe^{2+} and subsequent reprecipitation of Fe^{2+} to Fe^{3+}, in the lighted stream channel could increase the chance for adsorption or coprecipitation of $^{32}PO4$ in streamwater with newly formed iron complexes in the suspended-solids fraction. This faster turnover might explain the increase in the ^{32}P associated with the suspended solids in the lighted sites. Iron concentrations in suspended solids have yet to be analyzed so as to provide additional information to help interpret these results.

Algae actively removed ^{32}PO directly from the water column in St. Kevin Gulch. This removal is demonstrated by the greater concentration of ^{32}P in algae and ATP extracts of algae (table 2) compared to iron oxides. Although the concentration of ^{32}P in the ATP extract (table 2) has not been normalized by ATP biomass, this result provides evidence that ^{32}P actually enters the algal cells rather than adsorbing onto the hydrous iron oxides coating the cells. Also, the greater APA in algae during the day indicates that algae probably were responding to the increased demand for P when photosynthesis occurs. The potential for greater turnover of P during the day due to photoreduction of hydrous iron oxides releasing sorbed phosphate (Franko and Heath, 1982) could result in more P being available to algal cells and greater APA activity during the day.

The calculation of ^{32}P in algae and hydrous iron oxides per unit streambed area (table 3) provides an estimate of the proportion of $^{32}PO4$ added to the stream entering the different components. At the two upstream sections, more of the ^{32}P was associated with the hydrous iron oxides, whereas at the two downstream sections (table 3; Bio 2 to Bio 3 and Bio 3 to Bio 4), more ^{32}P was associated with the algal component (table 3). Although algae had larger concentrations of ^{32}P per mass compared to hydrous iron oxides at the two upstream sites, algae had less mass per unit area than hydrous iron oxides (table 2). Thus, the high percent cover (table 3; 0 m to Bio 1) and heavy mass per area (table 2; Bio 1 to Bio 2) of hydrous iron oxides were important weighing factors that determine the quantitiy of ^{32}P in hydrous iron oxides at the two upstream sites. Regardless, algae and hydrous iron oxides are important sinks for phosphate in the stream channel.

SUMMARY

Algae compete successfully with the abiotic pathways (adsorption of phosphate onto hydrous iron oxides) for available phosphate in streams contaminated by acid mine drainage. Algae remove phosphate from the water as indicated by the downstream decrease of concentrations of ^{32}P in water. Phosphate then is incorporated into algal cells as demonstrated by ^{32}P in algae and ^{32}P in ATP extracts of algae. Algae produce greater quantities of acid phosphatase during the day to obtain more phosphate during this period of greatest photosynthetic activity (greatest demand for P). Algae and hydrous iron oxides are important sinks for phosphate in St. Kevin Gulch as indicated by the quantities of ^{32}P in each of these components of the stream channel. The extensive growth of algae observed during August in St. Kevin Gulch and represented by algal cover in this study indicates that algae can successfully obtain P for growth, and that at present P probably is not a limiting nutrient.

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TRANSITION METAL GEOCHEMISTRY OF THE UPPER ARKANSAS RIVER, COLORADO

By Edward Callender[1], Briant A. Kimball[2], *and* Ellen V. Axtmann[3]

ABSTRACT

Whole water and bottom sediment samples were collected along the length of the Upper Arkansas River in south-central Colorado in October 1988 and May 1989. Water samples were filtered at several pore sizes and sediment samples were sieved through a 60- micrometer screen. Water samples were analyzed for dissolved and particulate iron, manganese, and zinc, whereas sediment samples were analyzed for the same elements contained in an extractable and total sedimentary phase.

During a period of low flow (October), the concentration of dissolved iron appears to be controlled by equilibrium with amorphous iron phases, and the manganese and zinc partitions to the particulate fraction in the downstream direction. Under high flow conditions (May), the distribution patterns of all three metals are controlled by physical factors, such as discharge and turbulence.

The downstream attenuation of sedimentary iron, manganese, and zinc follow different patterns. Iron is added to the river sediments by acid mine drainage near Leadville and there is no increase or sustained partitioning of iron to the sediment downstream. Manganese and zinc are also contributed by contaminant inflows near Leadville but appear to be reacting between the water column and bed sediment in a downstream direction. A substantial fraction of these sedimentary metals is present as an easily extractable phase. Iron occurs mostly in the mineral fraction of the bed sediment.

INTRODUCTION

Metal rich, acidic water drains from mines and tailings piles in the Leadville, Colo., area. As acid streams enter the Arkansas River, which has a pH of approximately 8, colloidal iron oxyhydroxide precipitates from, and is transported in suspension. These colloids are transported downriver to Pueblo Reservoir (located upstream from Pueblo in fig. 1) and appear to accumulate in the reservoir bottom sediments (Callender and others, 1989). In 1983 and 1985, several thousand liters of metal rich water flowed from mine drainage tunnels, and colloids were visibly traced downstream from Leadville for about 100 km (kilometers). The colloids accumulate as distinct reddish orange bands that can be observed in sediment cores from Pueblo Reservoir. The transport of iron colloids in the river probably is rapid in order that they accumulate as distinct seasonal bands in the sediment cores. The purpose of this paper is to describe the transport and deposition of colloidal metals that originate from acid mine drainage near Leadville.

Metals were sampled as dissolved ions, suspended particulates, or colloids; as part of sediment coatings; and as part of the total bulk sediment. A 250-km reach of the Arkansas River, downstream from Leadville to the Pueblo Reservoir, was sampled (fig. 1). In addition, major tributaries were sampled to evaluate the effects of inflows of water and sediment.

METHODS

The sampling procedure for water and bed sediments was designed to investigate the extent of colloid transport and the interactions of colloids with dissolved metals and bed sediments downstream from Leadville. The main hypothesis to be tested was that metals, particularly cadmium (Cd), copper (Cu), iron (Fe), manganese (Mn), lead (Pb), and zinc (Zn), are derived from acid mine drainage in the Leadville area and are distributed downstream in a pattern representing attenuation from the source. In order to test this hypothesis, water column and bed sediment samples were collected at 12 mainstream gaging stations and 10 major tributary inputs downstream from Leadville in October 1988. In May 1989, six mainstream stations and five tributary inputs were sampled. Base flow conditions were represented by the October 1988 samples and snowmelt runoff (high flow conditions) were represented by the May 1989 samples.

Water samples were collected by a discharge integrating method and processed using multiple filter pore size membranes. First, an unfiltered sample was acidified to represent the acid-soluble metal concentration. The purpose of this sample was to digest the colloidal iron oxyhydroxide material. In water samples collected near acid mine drainage inputs, the addition of reagent acid dissolved most of the particulate material. However, downstream from Leadville, there are increasing quantities of suspended sediment composed of aluminosilicate phases that were not easily attacked by reagent acid. A split of the whole water sample was filtered using a 100,000 molecular weight nominal pore-size membrane. This filtrate represented the truly dissolved metal concentrations. The particulate metal concentrations represent the difference between the acidified, unfiltered concentrations and the dissolved concentrations defined above.

Solid phase samples were collected during both sampling trips. Bottom sediment was collected from pooled areas and bars and sieved in the field through a nylon 60-μm (micrometer) screen. During high-flow conditions, suspended sediment was collected from cableways at qaging stations. Approximately 50 liters of water provided enough suspended sediment for chemical analysis.

Dissolved and total metal samples were acidified with doubly distilled nitric acid and analyzed with a model 975 Jarrel-Ash[4] inductively coupled plasma (ICP) spectrometer. For total chemical analysis, sediment samples were digested by a combination of nitric, hydrofluoric, and perchloric

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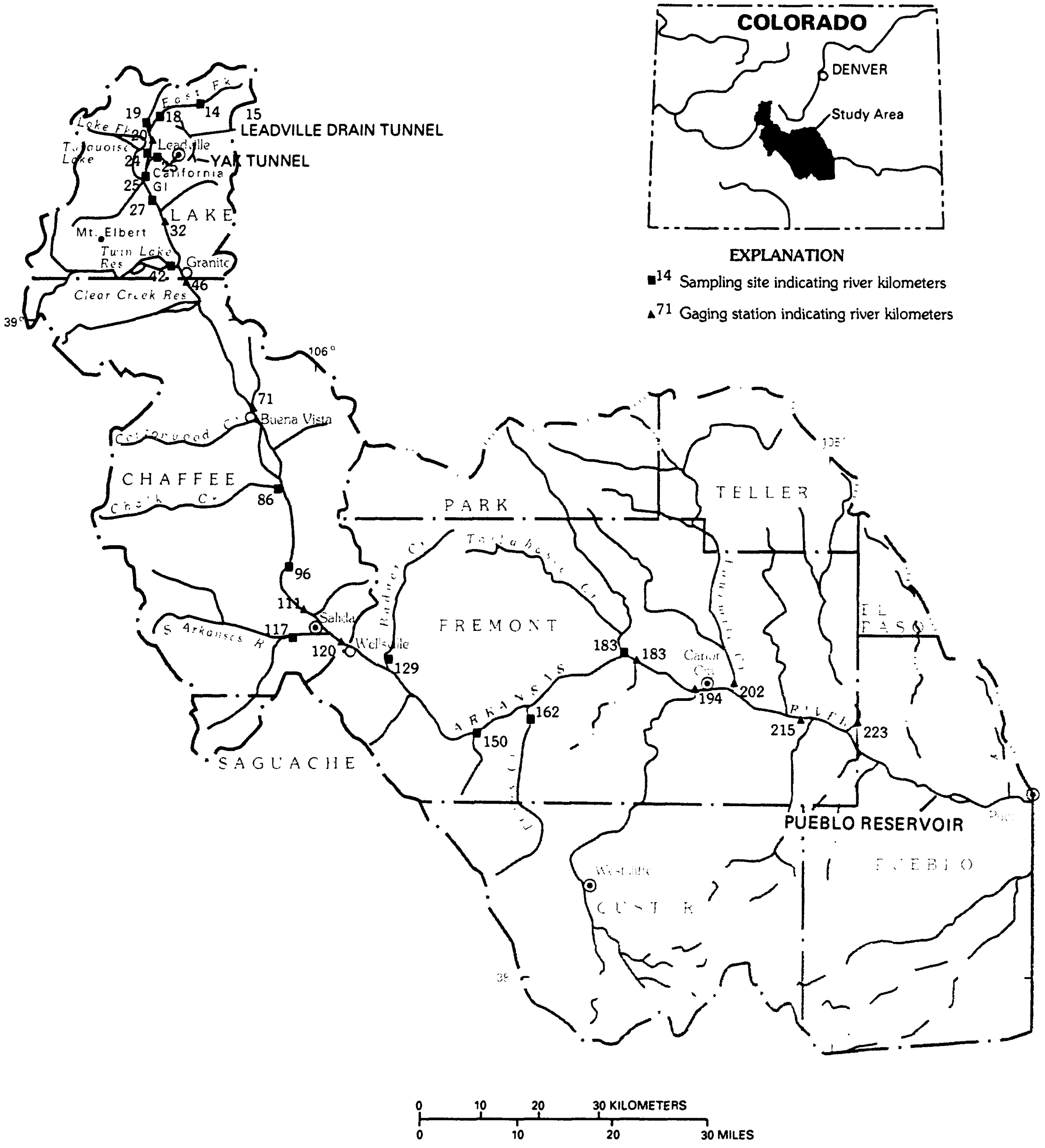
COLORADO
DENVER
Study Area
EXPLANATION
■14 Sampling site indicating river kilometers
▲71 Gaging station indicating river kilometers
East Fk
19
18
14
15
LEADVILLE DRAIN TUNNEL
Lake Fk
20
Turquoise Lake
Leadville
YAK TUNNEL
24
25
California Gl
25
27
LAKE
Mt. Elbert
32
Twin Lake Res
42
Granite
46
Clear Creek Res
39°
106°
71
Buena Vista
Cottonwood Cr
CHAFFEE
Chalk Cr
86
96
111
Salida
S Arkansas R
117
120
Wellsville
129
PARK
FREMONT
Tallahassee Cr
183
183
Canon City
194
202
ARKANSAS
162
150
215
223
TELLER
EL PASO
105°
SAGUACHE
PUEBLO RESERVOIR
PUEBLO
CUSTER
Westcliffe
38°
0 10 20 30 KILOMETERS
0 10 20 30 MILES

Figure 1. Map of the upper Arkansas River, Colorado, drainage basin showing the study area.

acids, and the extracts were analyzed by atomic emission spectrometry-inductively coupled plasma (AES-ICP) (Lichte and others, 1987). To determine the quantity of Fe, Mn, and Zn associated with sedimentary ferromanganese oxydroxides, a slurry of sieved, moist bed material was extracted with a mixture of 1 molar hydroxylamine hydrochloride and 25 percent acetic acid (Chester and Hughes, 1967). Filtered extracts (0.2 µm) were analyzed by flame atomic absorption spectrophotometry and AES-ICP.

RESULTS

The concentration of dissolved and particulate Fe, Mn, and Zn were multiplied by the instantaneous discharge of the river at any given station to compute load. The calculated loads are plotted in figures 2A through 2C. Decreases in dissolved and particulate (Fe and Mn) loads at river kilometer 194 in October 1988 result from an actual decrease in discharge from diversions upstream of the sampling site. For October 1988, 12 mainstream stations were sampled and for May 1989, 6 mainstream stations were sampled. For the October sampling under low flow conditions, particulate Fe load is at least 10 times greater than dissolved Fe load (fig. 2A). The dissolved Fe concentration is relatively constant, and changes in load reflect changes in discharge. The above observations are also true for the Fe distributions in May 1989, when the increased loads reflected increased discharges. There are major sources of particulate Fe entering the Arkansas River at California Gulch (CG 99, river kilometer 25), Chalk Creek (CH 40, river kilometer 86), and Fourmile Creek (FM 40, river kilometer 201), and the particulate Fe load is nearly constant downstream from the upper two inflows for the October sampling period.

The dissolved Mn loads are greater than the particulate loads (fig. 2B). The load of dissolved Mn is high and the load of particulate Mn is low in the reach from river kilometer 25 to 100. Below river kilometer 125, both loads are approximately equal. For high flow conditions during May 1989, the dissolved Mn load decreases from its source at river kilometer 25 downstream to river kilometer 220 (fig. 2B). In contrast, particulate Mn increases downstream from river kilometer 32.

The downstream distribution of Zn loads is similar to that for Mn. For the low flow period in October 1988, the load of dissolved Zn is 10 times greater than that for particulate Zn (fig. 2C). During high flow conditions (May 1989), the pattern in Zn loads is different downstream from river kilometer 32 in that the particulate loads are greater than the dissolved loads in a downstream direction.

For the October 1988 sampling period, there is a strong attenuation in the concentration of total sedimentary Fe downriver from California Gulch (river kilometer 25) to background levels below river kilometer 48 (fig. 3A). In figure 3, points representing river locations are connected, and points representing tributaries are scattered. The background levels reflect the Fe concentration in sediment contributed by the tributary inflows. Extractable Fe also decreases sharply in a downriver direction. This pattern is similar to that observed for the extractable sedimentary Fe contributed by tributary inflows (fig. 3A). Tributary sedimentary Fe concentrations are approximately equal to mainstream sedimentary Fe concentrations. These Fe concentrations are typical of those in the local geological source material. The patterns for sedimentary Fe sampled in May 1989 are similar to those described above (fig. 3A).

Total and extractable sedimentary Mn increases in the reach from river kilometer 25 through 110 (fig. 3B). This is reflected in both the October and May distributions. For October, there is strong attenuation in Mn from the source at river kilometer 20 to 32 and moderate attenuation downriver from river kilometer 71 (fig. 3B). For May, the major input of sedimentary Mn to the river is California Gulch (river kilometer 25) rather than upstream sources as indicated by the October data (fig. 3B). There is a marked decrease in total sedimentary Mn below river kilometer 32 for the May sampling period. The percentage of extractable Mn is less below river kilometer 111 for both sampling periods (fig. 4). By contrast, the sedimentary Zn distribution (fig. 3C) shows a strong attenuation below California Gulch (river kilometer 25) for October and below river kilometer 32 for May. In October, the percent extractable sedimentary Zn remains essentially constant throughout the reach of the Arkansas River that was sampled (fig. 4). In May, extractable Zn decreased downriver from river kilometer 111.

The October distributions of total sedimentary Fe and Zn show a similar pattern and the May distributions of total and extractable Mn and Zn exhibit similar patterns.

DISCUSSION

The distribution of dissolved Fe load (fig. 2A) in the upper Arkansas River for the October sampling period parallels the downstream pattern of discharge because dissolved Fe concentrations remain nearly constant. A constant dissolved Fe concentration, despite dilution by tributary inflows, suggests that the concentration is determined by equilibrium with amorphous iron phases. The dissolved Fe loading pattern for the May sampling period is controlled by discharge in that loads increase somewhat downstream while concentrations decrease. The distribution of total sedimentary Fe (fig. 3A) suggests a point-source input of Fe at river kilometer 25 (California Gulch, CG 99) and strong attenuation downstream. This input consists of amorphous to poorly crystalline iron oxyhydroxide--a conclusion that is supported by the extractability data (fig. 4).

Under low flow conditions (October 1988), dissolved Mn load predominates upstream of river kilometer 110 (fig. 2B) and is approximately equal to particulate Mn load downstream. It is apparent that Mn partitions to the particulate fraction in the downstream direction and that there may be loss of Mn from the water column, indicated by the overall reduction in Mn loads. The increase in particulate Mn below km 110 may be the result of surface reaction with colloidal iron oxyhydroxide. Ferric-oxyhydroxide precipitates are known to catalyze the oxidation of manganous Mn (Sung and Morgan, 1981). The downstream profile of particulate Fe loads indicates that colloidal or particulate Fe mostly remains in suspension over the entire 250-km reach of the river. This is consistent with finding

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[4] The use of brand names is for identification purposes only and does not constitute endorsement by U.S. Geological Survey.

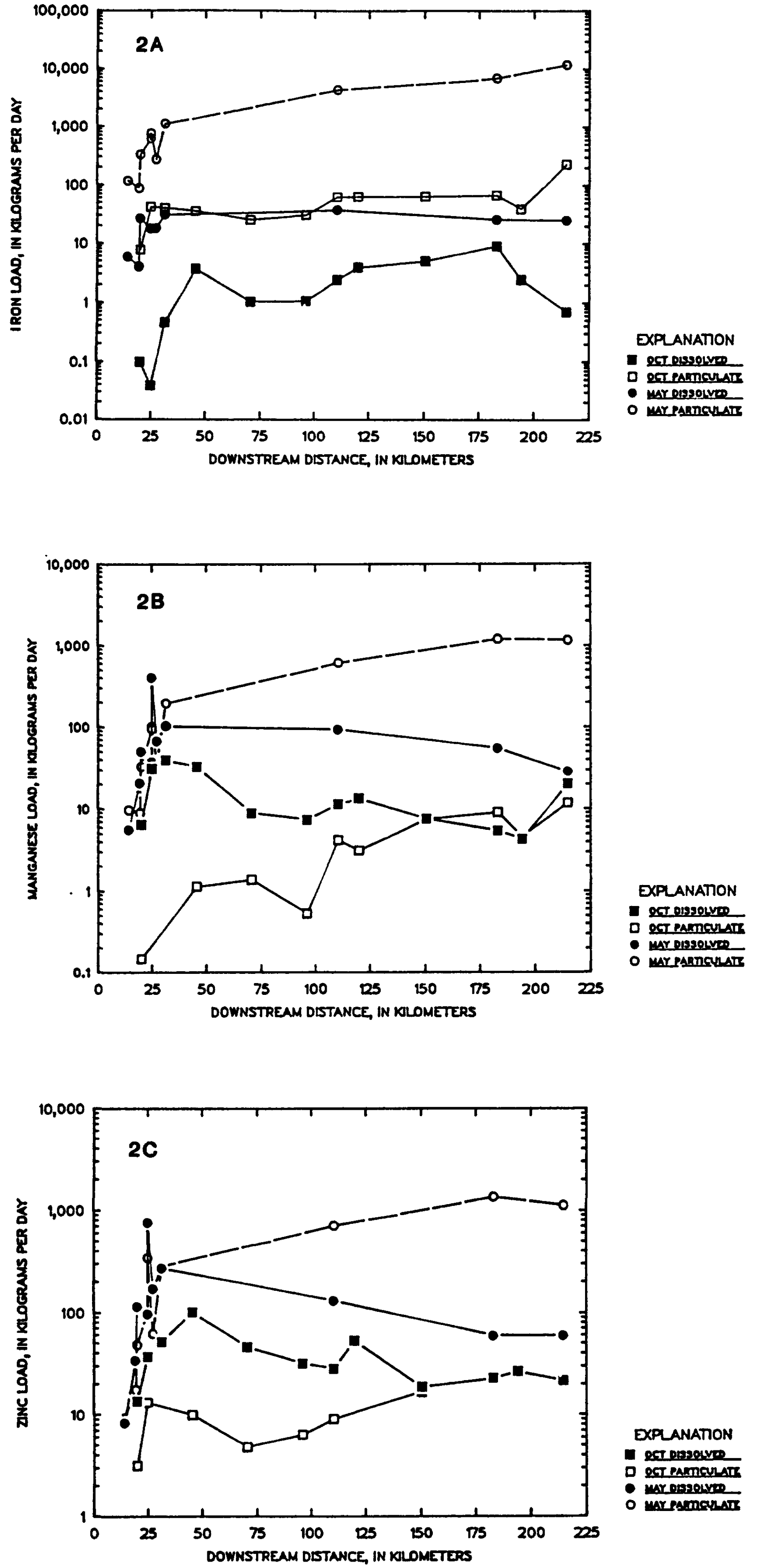

Figure 2. Longitudinal distribution of dissolved and particulate metal load in the upper Arkansas River, Colorado, during the October 1988 and May 1989 sampling periods. A. Iron B. Manganese C. Zinc.

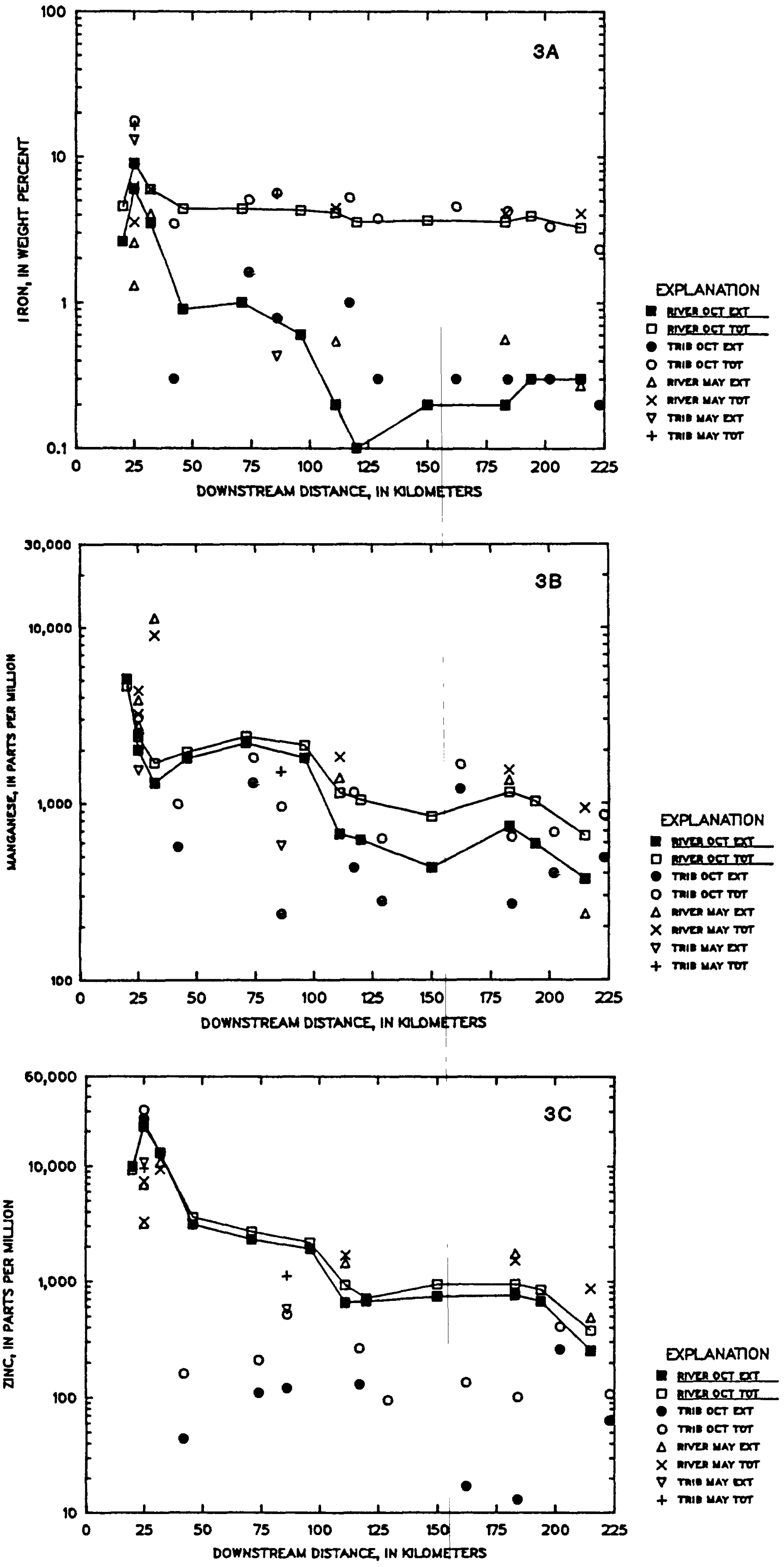

Figure 3. Longitudinal distribution of sedimentary metals in bed material from the upper Arkansas River, Colorado. The plotted data includes total and extractable analyses for main stem and tributary samples collected during the October 1988 and May 1989 sampling periods.

orange banding in Pueblo Reservoir sediments that represent breakouts of metal rich waters from mine drainage tunnels. Apparently, the long residence time of colloidal or particulate Fe aids the conversion of dissolved to particulate Mn downstream. The broad peak in sedimentary Mn concentrations upstream from river kilometer 110 (fig. 3B) suggests that Mn is reacting with sediments. A substantial loss of dissolved Mn occurs in this reach (river kilometer 30 to 100) of the river, and sediments sampled from the reach contain more extractable Mn than do sediments sampled downstream (fig. 3B). The geological sources of tributary sediments contain much less extractable Mn than do the river sediments (fig. 3B), and, thus, without a contribution of reactive Mn from the water column, simple dilution would reduce the concentrations of Mn in river sediment.

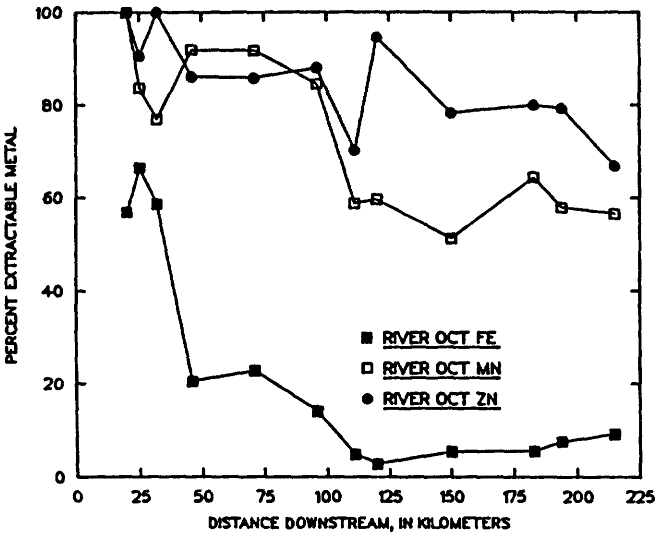

Figure 4. Longitudinal distribution of percent extractable iron, manganese, and zinc in bed material collected from the upper Arkansas River, Colorado, during the October 1988 sampling period.

Under high flow conditions (May 1989), there is a strong separation between dissolved (lower) and particulate (higher) Mn loads (fig. 2B), possibly because of resuspension of bed sediments that contain appreciable quantities of surface-reactive Mn. The method used for preserving a total water sample involves the addition of nitric acid that can easily solubilize surface-reactive Mn. A similar explanation can be used to explain the separation between dissolved and particulate Zn at high flow (fig. 2C).

The distribution of dissolved and particulate Zn loads for the October 1988 sampling period exhibits a somewhat parallel pattern downstream (fig. 2C) with the exception of the sample from river kilometer 150. This pattern is in contrast to the October 1988 distribution of dissolved and particulate Mn (fig. 2B), suggesting that Zn is reacting with sediments more uniformly than is Mn in the upper Arkansas River. The sedimentary Zn data, which indicate that extractability is consistently high for all sampling sites (fig. 4), support this conclusion. Because of the nature of the extraction, much of the Zn is associated with oxyhydroxides of Fe and Mn. The Zn concentrations of geologic source material contributed by tributary inputs are approximately 10 percent of river sediment concentrations (fig. 3C); much of the sedimentary Zn is in a reactive phase.

CONCLUSIONS

The downstream attenuation of extractable Fe, Mn, and Zn in bed sediment follows different patterns. These patterns reflect the multiple processes that affect metal transport. The Fe- attenuation pattern (fig. 3A) suggests that Fe is added to the river sediments by acid mine drainage near Leadville, and that there is no increase or sustained partitioning of Fe to the sediment downstream. These observations indicate that there is little interaction between dissolved and colloidal Fe and the bed sediments. Mn and Zn (figs. 3 B,C) are also contributed by contaminant inflows near Leadville but appear to be involved in reactions between the water column and bed sediment in the river reach downstream from Leadville. Both Mn and Zn, which partition predominantly to the dissolved phase in the water column above river kilometer 150 (figs. 2 B,C), occur as a substantial fraction of extractable metals in the bed sediment (fig. 4). Fe, which partitions to the particulate phase in the water column, is mostly in the mineral fraction of the bed sediment (fig. 4). These observations are consistent with a conservative attenuation pattern for Fe and a reactive pattern for Mn and Zn in bed sediment.

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USE OF ENVIRONMENTAL VARIABLES TO ESTIMATE METAL LOADS IN STREAMS, UPPER ARKANSAS RIVER BASIN, COLORADO

By Gregory A. Wetherbee[1] *and* Briant A. Kimball[2]

ABSTRACT

Knowledge of processes controlling metal loads aids in the estimation of metal loads at streamflow-gaging stations as well as the abatement of metal contamination in streams. Stream discharge commonly is used as an estimator of loads of conservative constituents, but metals are reactive and affected by many factors in addition to discharge. Numerous hydraulic, chemical, physical, and biological processes contribute to the variability of metal loads in streams. Environmental variables including discharge, pH, alkalinity, total organic carbon concentration, sulfate concentration, iron colloid concentration, and temperature were used in multiple linear regression models to estimate total iron, manganese, zinc, cadmium, and calcium loads in the headwaters of the upper Arkansas River. Data from two sampling locations on tributaries affected by mine drainage and two sampling locations on the main stem of the Arkansas River were analyzed. The concentration of iron colloids described a significant amount of the variation in total iron, manganese, zinc, and cadmium loads at three of the four sampling locations, and seasonal variation in the significance of colloid concentration was indicated. No two models for predicting metal loads were identical, indicating that local variations in water chemistry and environmental processes affect metal loads. Although no unique and transferable combination of processes control metal loads, discharge and iron colloid concentration are important.

INTRODUCTION

Several tributaries to the upper Arkansas River are contaminated by acid mine drainage. These tributaries add large quantities of heavy metals to the Arkansas River in the Leadville, Colo., area (fig. 1). Numerous hydraulic, chemical, physical, and biological processes contribute to the variability of metal loads in streams. Knowledge of the processes that affect metal loads aids in the estimation of transition-metal loads at streamflow-gaging stations and the abatement of metal contamination in streams.

Stream discharge commonly is used as a predictor of major constituent loads. However, transition metals generally have a much less-defined relation to stream discharge. The changing predominance of different sources of metals, variability of pH and redox conditions, the type and quantity of complexing agents, fluctuations in sediment concentration, biological activity, and temperature affect the instantaneous concentration of metals in streams (Forstner and Wittmann, 1979). This paper addresses the relative importance of environmental variables associated with processes that affect the variability of transition metal loads in streams in the Leadville area and provides insight into the problem of estimating transition-metal loads at streamflow-gaging stations.

Data were collected during 1986-89 at sampling sites in the upper Arkansas River basin near Leadville, Colo. (fig. 1). Detailed analysis of data collected at the AR05, AR65, CG99, and LD10 sites are presented herein. The two sites labeled AR05 and AR65 in figure 1 are on the Arkansas River and the two sites labeled LD10 and CG99 are on mine-drainage tributaries to the Arkansas River. Instantaneous discharge, water-quality samples, and other hydrologic data were collected at these sites. Sampling was designed to evaluate seasonal and spatial hydrologic trends in the study area. All flow and seasonal conditions are assumed to be represented because monthly and some biweekly data were collected during the 8-month period of greatest annual hydrograph variation.

METHODS

Data for this study include instantaneous discharge measurements and water-quality analyses. Discharge was measured with current meters described in Buchanan and Somers (1980). Water samples were collected by the equal transit rate method (Guy and Norman, 1982, p. 28), and water temperature, specific conductance, pH, and alkalinity were measured. Acidified whole-water samples were analyzed for acid-soluble metal concentrations, and dissolved metal concentrations were obtained from samples filtered through a 0.10-μm (micrometer) filter. The term dissolved is used operationally because some colloidal material can pass through the 0.10-μm filter.

The properties of amorphous iron hydroxide colloids in streams containing acidic mine drainage have been documented by Ranville and others (1989). Iron colloid concentration was calculated for each sample as follows:

$$\text{Iron colloid concentration} = [\mathrm{FeT}] - [\mathrm{FeD}] \qquad (1)$$

where

[FeT] = acid-soluble iron concentration from whole-water sample; and
[FeD] = dissolved iron concentration.

Iron colloid concentration also might be defined as particulate iron concentration; however, suspended sediment concentration data indicate that suspended sediment concentrations are very low in these streams. Therefore, it is reasonable to assume that the iron colloid concentration does not include iron in suspended sediment. The effect of iron colloids on in-stream metal chemistry in the upper Arkansas River was reported by Kimball and Wetherbee (1989). These colloids adsorb metals and might coprecipitate metals in streams (Smith and others, 1989). Major point sources of zinc input to the Arkansas River also are major sources of iron colloids (fig. 2). Therefore, iron colloid concentration was incorporated into the statistical modeling to include data

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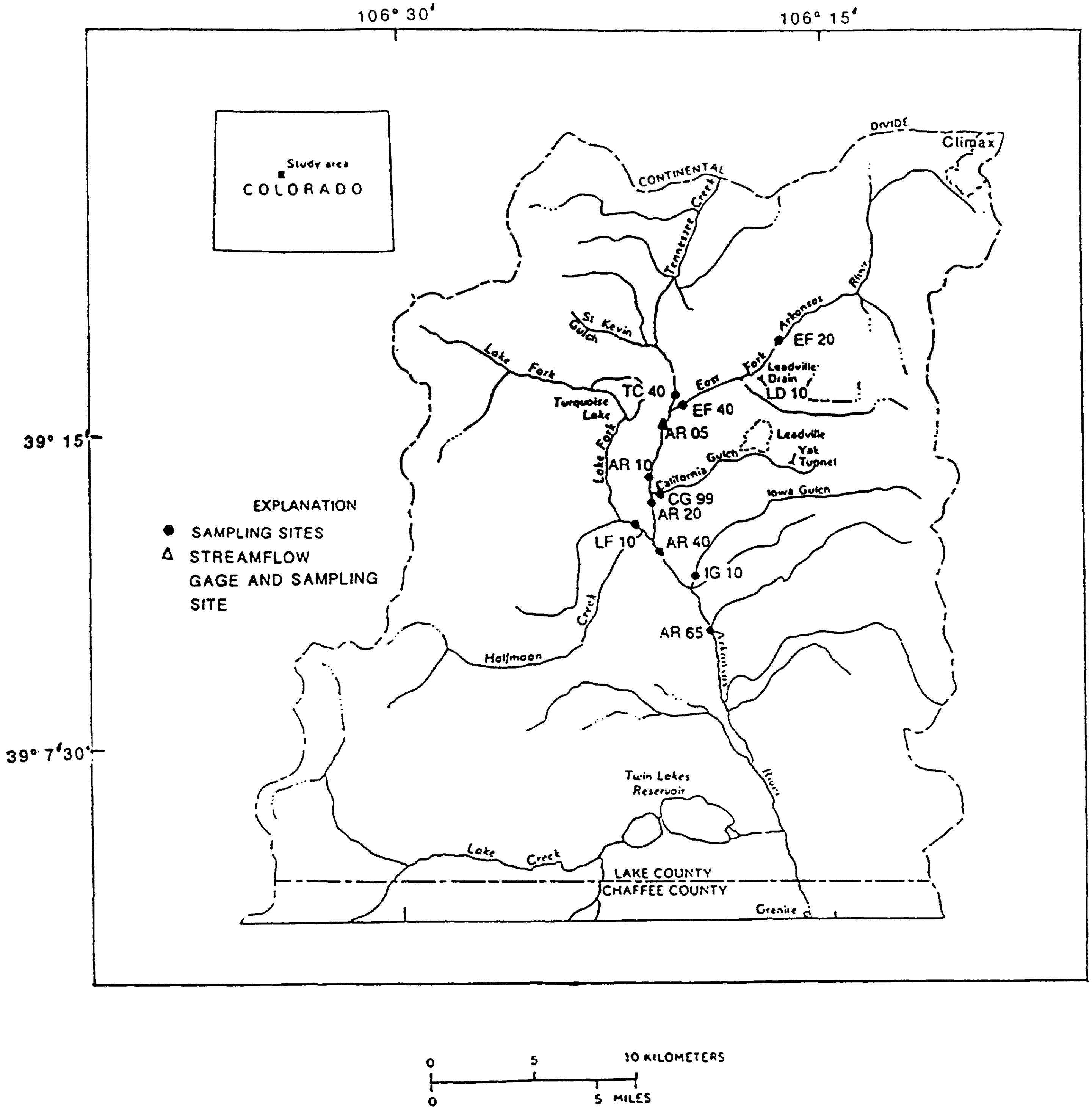
106° 30'
106° 15'
39° 15'
39° 7'30"
Study area
COLORADO
EXPLANATION
● SAMPLING SITES
Δ STREAMFLOW GAGE AND SAMPLING SITE
Divide
Climax
Continental
Tennessee Creek
St Kevin Gulch
Lake Fork
Turquoise Lake
TC 40
East Fork
Arkansas River
EF 20
EF 40
Leadville Drain
LD 10
AR 05
Leadville
Yak Tunnel
California Gulch
AR 10
CG 99
AR 20
Iowa Gulch
LF 10
AR 40
IG 10
Lake Creek
AR 65
Halfmoon
Twin Lakes Reservoir
Lake Creek
LAKE COUNTY
CHAFFEE COUNTY
Granite
0 5 10 KILOMETERS
0 5 MILES

Figure 1. *Location of study area and sampling sites. (Modified from Kimball and Wetherbee, 1989, fig. B-4.)*

assumed to be representative of sorption processes or the major point source contributors to the metal load in the Arkansas River or both.

In the analysis contained herein, instantaneous total constituent loads were calculated by multiplying instantaneous discharge by constituent concentrations obtained from samples that accompanied the discharge measurements. Discharge, pH, alkalinity (buffering capacity), water temperature, and concentrations of sulfate, total organic carbon, and iron colloids were used as regressors to predict instantaneous metal loads in multiple linear regression models. Mallow's Cp statistic was used to determine the best multiple linear regression models to predict loads for calcium, cadmium, iron, manganese, and

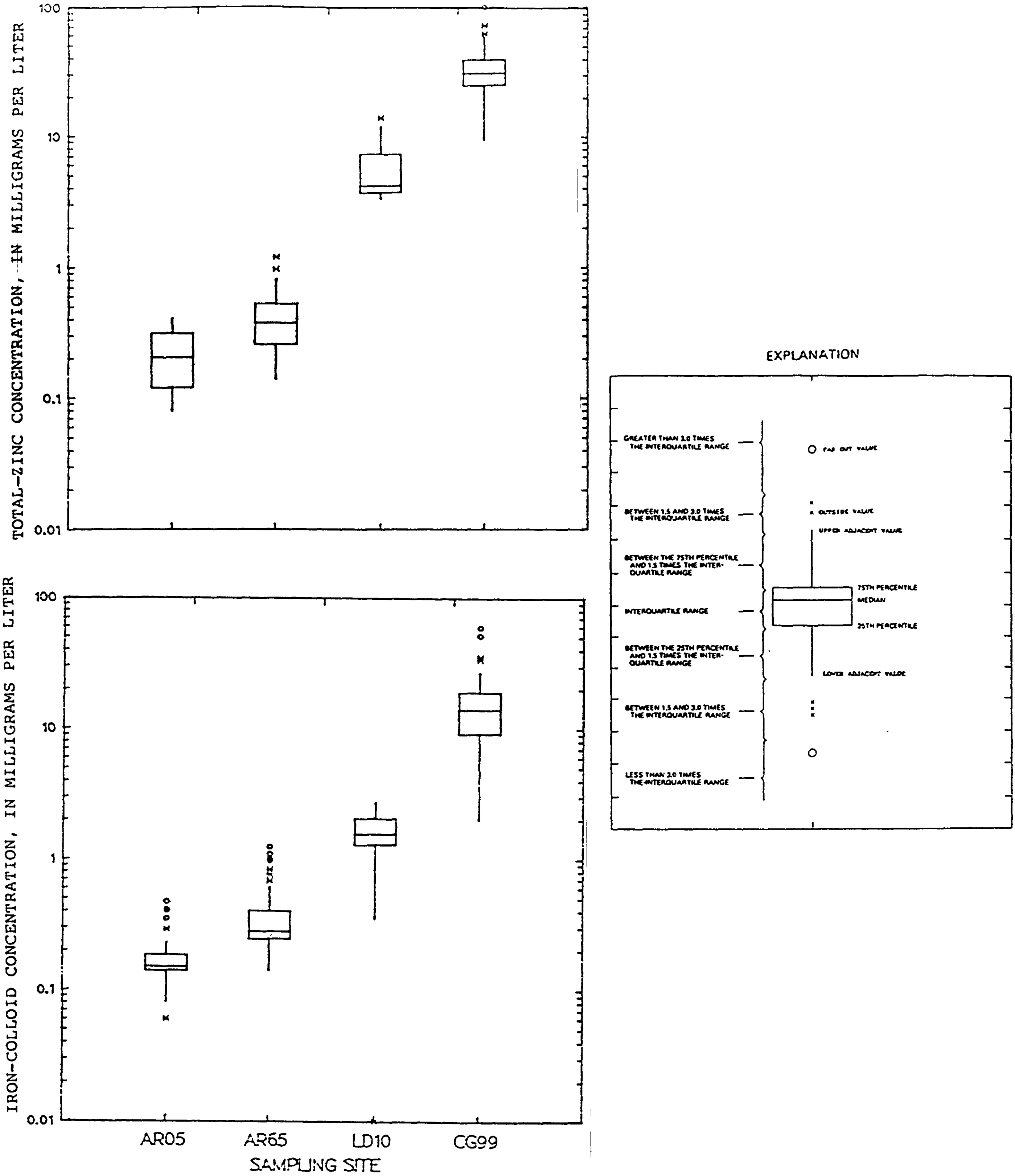

Figure 2. *Boxplots of total-zinc and iron-colloid concentrations for sampling sites AR05, AR65, LD10, and CG99.*

zinc. Mallow's Cp statistic incorporates the number of observations, the number of coefficients, the mean square error, and the true error of the regression models to achieve a compromise between bias minimization and minimization of the variance of the estimator (Montgomery and Peck, 1982, p. 252). Colinearity of regressors for the regression models was tested with the variance inflation factor (Montgomery and Peck, 1982, p. 299). Seasonal variation in metal loads and associated load-controlling processes were accounted for by analyzing the data for the rising limb of the annual hydrograph independently from the data for the falling limb of the annual hydrograph. Results of these limb separation models were compared with models for which no seasonal variation or hysteresis was assumed. The variability in metal load described by each regressor implied the relative importance of processes controlling metal loads.

RESULTS

By plotting constituent discharge as a function of stream discharge, the amount of variation in constituent discharge described by stream discharge can be qualified. Because stream discharge is used to compute constituent discharge, stream discharge often describes a substantial amount of the variation in the constituent discharge. This situation is true for a conservative major ion constituent such as calcium. Data in figure 3 indicate a strong linear relation between total calcium discharge and stream discharge for sites AR05, AR65, and CG99; and a somewhat weaker relation for site LD10. There is very little variation in stream discharge at site LD10 because the site LD10 stream discharge is controlled by a pump. Although stream discharge is the dominant factor in controlling calcium discharge, the relation is less obvious for zinc (fig. 4). A pattern of hysteresis is evident for site AR05, where a surge of zinc at high flow decreases with decreasing flow. For sites AR65 and CG99, there seems to be a reasonable relation between zinc discharge and stream discharge for the falling limb of the annual hydrograph and a weaker relation for the rising limb. These plots indicate that processes, in addition to variation in stream discharge, control zinc and other metal discharges in these streams.

Sorption of metals onto colloidal surfaces might contribute to the variability of metal loads. Mine-drainage streams in the Leadville area are enriched in iron colloids. These streams generally have small ratios of dissolved iron to total iron concentrations because most of the iron in the water column is colloidal or particulate rather than dissolved. Inflows of colloids to the Arkansas River scavenge dissolved metals causing partitioning to the solid phase (Kimball and Wetherbee, 1989). Dissolved iron in the main stem Arkansas River is affected by tributary inflows of either colloidal or dissolved iron (fig. 5). The inflow of colloidal iron from site LD10 decreases the relative quantity of dissolved iron in the Arkansas River approximately 4 kilometers downstream from the inflow. The inflow of colloidal iron from site CG99 also decreases the relative quantity of dissolved iron in the Arkansas River. Conversely, input of dissolved iron from tributaries represented by sites TC40, LF10, and IG10 increases the relative amount of dissolved iron in the Arkansas River (fig. 5). Results of multiple linear regression modeling (tables 1 and 2) indicate that iron colloid concentration describes a significant percentage of the variation in metal loads.

Results of the multiple linear regression modeling were used to estimate the relative importance of processes controlling metal loads and not to derive equations for predicting loads. Nonetheless, diagnostic statistics were used to evaluate the strength of the models. Colinearity among regressors in multiple regression weakens models, and therefore, the variance inflation factor (VIF) for each regressor in each model was used in part to judge the validity of the models. Severe problems with colinearity are observed when the VIF approaches 10 (D.R. Helsel, U.S. Geological Survey, oral commun., 1990). For the models described herein, no VIF in excess of 5.0 was observed, indicating minimal colinearity. The validity of model regressors was tested using the p-value of the Student's t-distribution to determine the level of confidence at which regressors were significant. All regressors were significant with at least 95 percent confidence (p-values less than 0.05) for the models that excluded separation of the rising and falling limbs of the annual hydrograph. Separate modeling of the rising and falling limbs of the annual hydrograph yielded some models that had regressors significant with confidence levels as small as 11 percent.

When seasonal variability associated with hydrograph limbs is ignored, iron colloid concentration is significant in every regression equation for sites AR05, AR65, and LD10 (table 1). Different models were developed at each site for each constituent, indicating that the results of no single model can be transferred to different sites because environmental factors that affect transition metal concentrations are site specific. However, iron colloid concentration describes from 4 to 75 percent of the variation in the transition-metal loads at sites AR05, AR65, and LD10. Models for cadmium at sites AR05 and AR65 should be qualified because most of the cadmium concentration data for sites AR05 and AR65 were at a level that challenged analytical limitations.

Iron colloid concentration is not predictive of metal transport at site CG99 where iron colloid concentration is very high. The CG99 site is located near the mouth of California Gulch, which contributes large quantities of metals and colloids to the Arkansas River. California Gulch receives water from many sources, including a publicly owned treatment works, and contribution of phosphate and organic carbon from this source might adsorb to the colloids or compete with them for metals (James Ranville, U.S. Geological Survey, oral commun., 1990). Discharge and sulfate concentration describes a significant amount of variation in transition metal loads in California Gulch (table 1).

Iron colloid concentration described more variation in the transition metal load than any other regressor for site LD10. Discharge at site LD10 is dominated by a pump, and therefore, load might be less affected by discharge. However, the total-calcium load at site LD10 and at the other sites is predominantly controlled by discharge. This strong relation between total-calcium load and discharge reflects the strong relation indicated in figure 2 and the conservative nature of calcium.

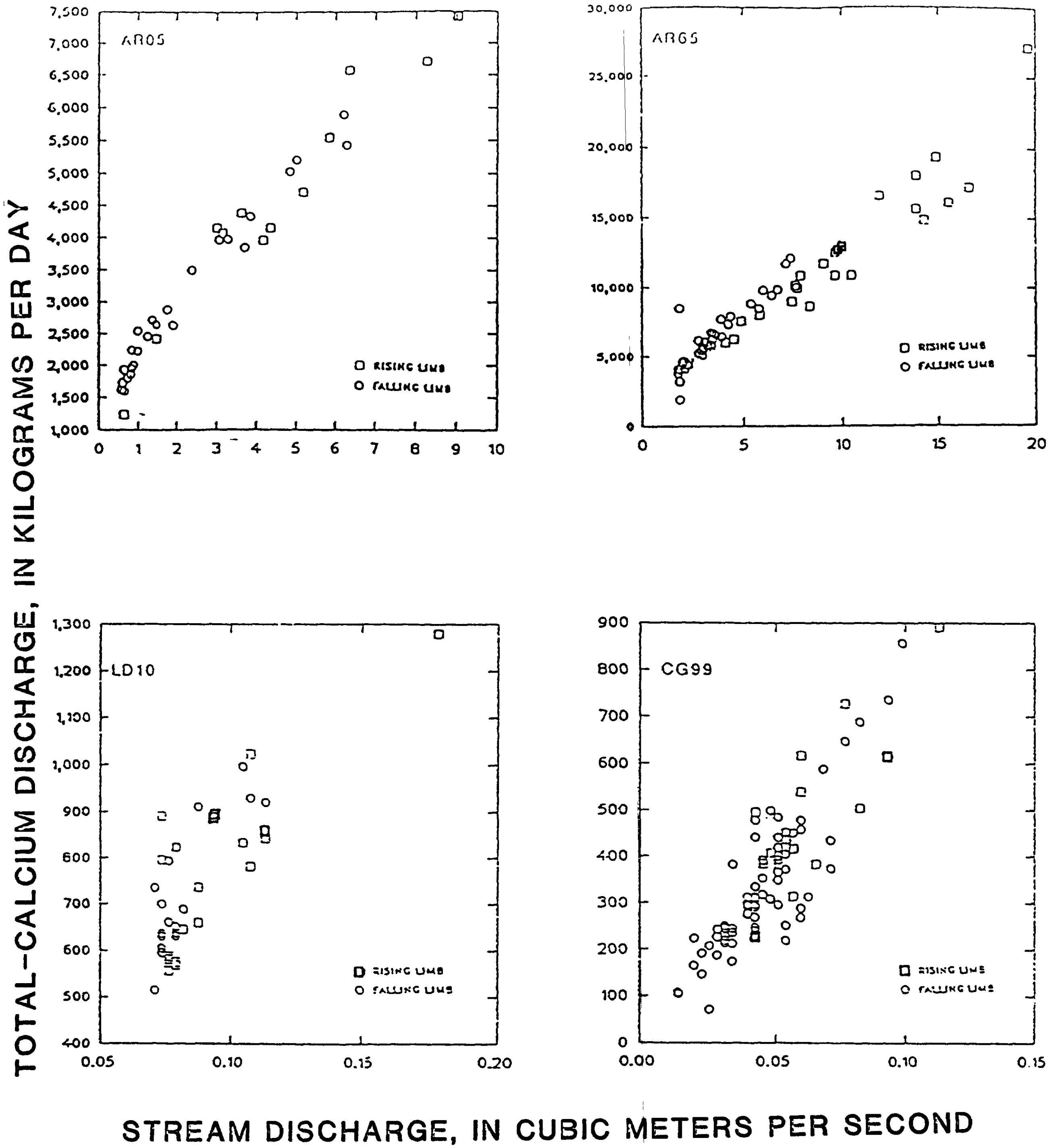

Figure 3. *Variation of total-calcium discharge with stream discharge for the rising and falling limbs of the annual hydrograph for sampling sites AR05, AR65, LD10, and CC99.*

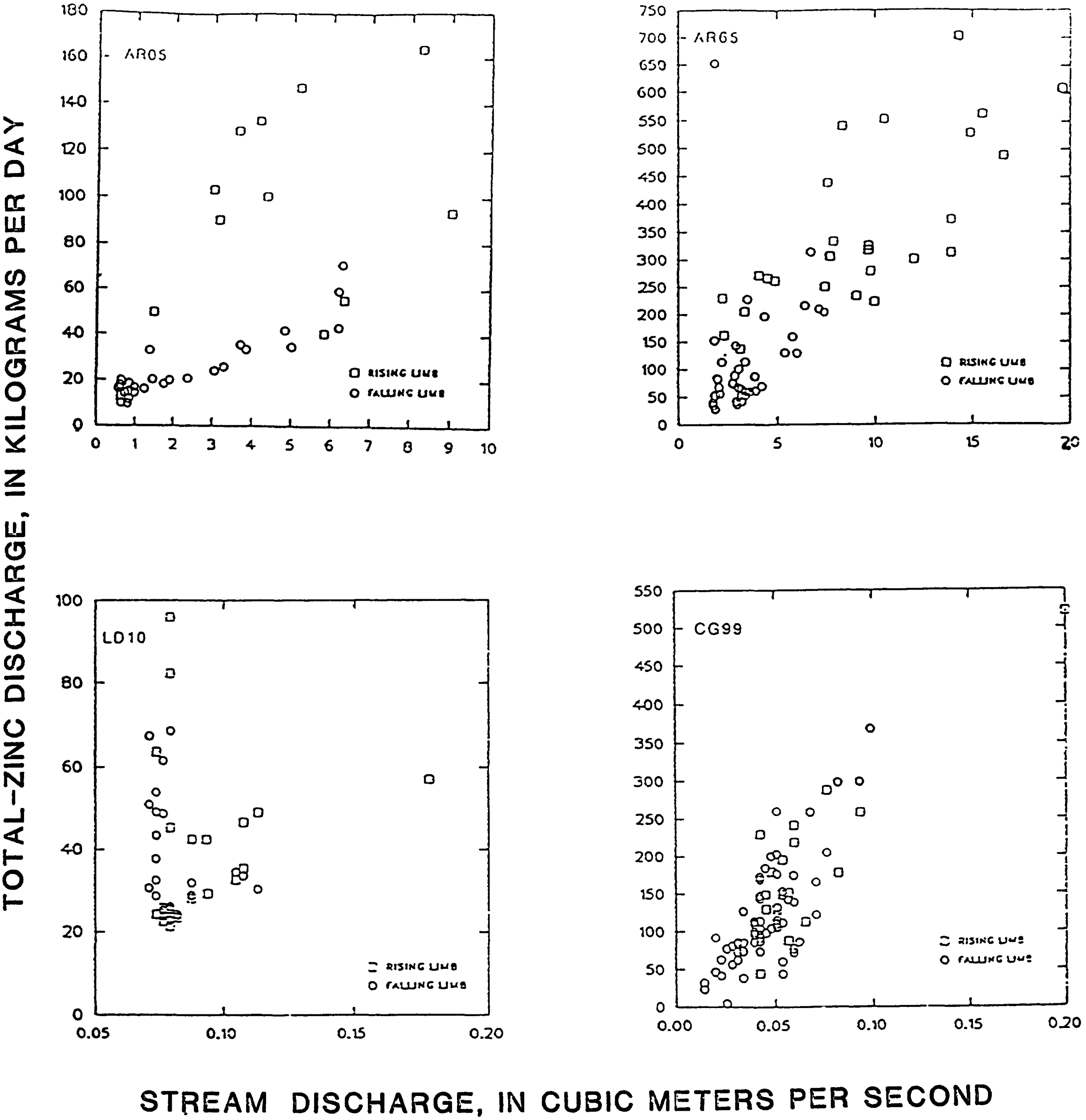

Figure 4. *Variation of total-zinc discharge with stream discharge for the rising and falling limbs of the annual hydrograph for sampling sites AR05, AR65, LD10, and CG99.*

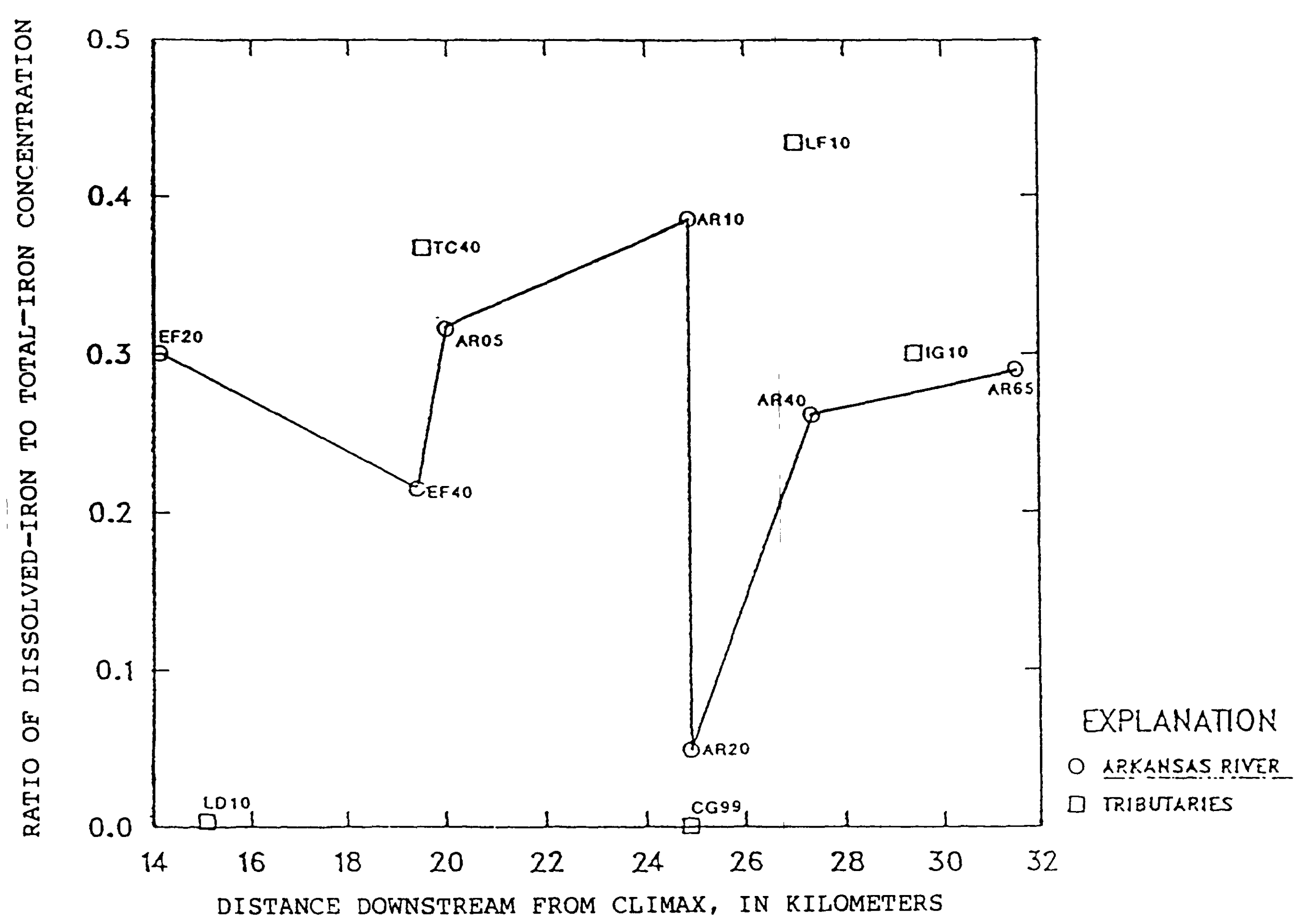

Figure 5. *Variation in ratio of dissolved-iron to total-iron concentration with downstream distance from Climax on July 21, 1989.*

Table 1. *Evaluation of best multiple linear regression models for selected total constituent loads*

[Partial r^2, amount of variation in total load described by independent variable; p-value, smallest level of significance allowing elimination of variable from model; Q, discharge; Col, iron-colloid concentration; Temp, water temperature; Alk, alkalinity; TOC, total-organic-carbon concentration; SO_4, sulfate concentration; Fe, iron; Mn, manganese; Zn, zinc; Cd, cadmium; Ca, calcium]

Dependent load variables	Diagnostic statistics for best multiple linear regression models											
	Sampling sites											
	AR05			AR65			CG99			LD10		
	Regressor	Partial r^2	p-value	Regressor	Partial r^2	p-value	Regressor	Partial r^2	p-value	Regressor	Partial r^2	p-value
Total Fe	Q	0.68	0.0001	Q	0.61	0.0001	Q	0.64	0.0001	Col	0.71	0.0001
	Col	.26	.0001	Col	.27	.0001	Col	.18	.0047	Q	.24	.0001
	Temp	.005	.0151				pH	.004	.0001	Alk	.005	.0264
	SO_4	.006	.0393									
Total Mn	Q	.63	.0001	Q	.65	.0001	Q	.62	.0001	Col	.61	.0001
	Col	.12	.0001	Col	.22	.0001	SO_4	.26	.0001	pH	.07	.0031
				Temp	.02	.0001						
Total Zn	Alk	.43	.0001	Q	.76	.0001	Q	.68	.0001	Col	.48	.0001
	Col	.11	.0050	Col	.04	.0001	SO_4	.23	.0001	Q	.07	.0101
				Temp	.08	.0001	Alk	.006	.0142	pH	.07	.0063
				Alk	.03	.0001						
Total Cd	Q	.54	.0001	Col	.75	.0001	Q	.55	.0001	Col	.41	.0001
	Col	.19	.0013	TOC	.14.	.0023	Alk	.12	.0001	pH	.16	.0001
Total Ca	Q	.96	.0001	Q	.93	.0001	Q	.87	.0001	Q	.55	.0001
	SO_4	.01	.0261	Alk	.007	.0118	Alk	.08	.0001	Col	.22	.0001
	Col	.004	.0296	Col	.005	.0234	Col	.005	.0047			

Table 2. *Evaluation of best multiple linear regression models for selected total constituent loads for rising and falling limbs of the annual hydrograph*

[Partial r^2, amount of variation in total load described by independent variable; p-value, smallest level of significance allowing elimination of variable from model; Q, discharge; Col, iron-colloid concentration; Temp, water temperature; Alk, alkalinity; SO_4, sulfate concentration; Fe, iron; Mn, manganese; Zn, zinc; Cd, cadmium; Ca, calcium; dashes indicate no appropriate model]

Dependent load variables	Diagnostic statistics for best multiple-linear-regression models											
	Sampling sites											
	AR05			AR65			CG99			LD10		
	Regressor	Partial r^2	p-value	Regressor	Partial r^2	p-value	Regressor	Partial r^2	p-value	Regressor	Partial r^2	p-value
Total Fe (rising limb)	Q	0.83	0.0001	Q	0.49	0.0104	Q	0.91	0.0001	Col	0.74	0.0001
	Col	.14	.0001	Temp	.37	.5451	Col	.03	.0001	Q	.24	.0001
				SO_4	.01	.5987	pH	.02	.0034			
				Alk	.02	.2450	Temp	.01	.0574			
				pH	.01	.8873						
Total Fe (falling limb)	Q	.80	.0001	Q	.51	.0001	Col	.57	.0001	Col	.68	.0001
	Col	.12	.0001	Col	.38	.0001	Q	.34	.0001	Q	.28	.0001
	Temp	.03	.0060	Temp	.01	.0188	SO_4	.01	.0152	Alk	.01	.0426
										SO_4	.01	.1610
Total Mn (rising limb)	Q	.59	.0079	Col	.52	.0001	Q	.65	.0001	SO_4	.67	.0001
	pH	.09	.1443	Q	.31	.0001	SO_4	.23	.0001	Q	.16	.0003
										pH	.04	.0310
Total Mn (falling limb)	Q	.85	.0001	Q	.57	.0001	Q	.53	.0001	Col	.81	.0001
	Col	.07	.0001	Temp	.17	.0001	SO_4	.39	.0001	pH	.05	.0121
				Col	.11	.0001	Col	.02	.0001			
				Alk	.01	.1079						
Total Zn (rising limb)	Q	0.19	0.3160	Q	0.60	0.0002	Q	0.77	0.0001	SO_4	0.52	0.0001
	pH	.26	.1815	Col	.14	.0004	SO_4	.12	.0004	Q	.22	.0007
				Alk	.08	.0043	pH	.04	.0700	pH	.06	.0388
							Col	.01	.1159			
Total Zn (falling limb)	Q	.82	.0001	Q	.54	.0001	Q	.54	.0001	Col	.67	.0001
	Col	.06	.0012	Temp	.30	.0001	SO_4	.37	.0001			
	Alk	.02	.0583	Col	.03	.0035						
Total Cd (rising limb)	--	--	--	--	--	--	Q	.51	.0013	SO_4	.47	.0002
							pH	.18	.0115	pH	.13	.0183
							SO_4	.09	.0006	Q	.10	.0306
							Col	.05	.0589			
Total Cd (falling limb)	Q	.82	.0001	--	--	--	Q	.46	.0001	Col	.52	.0001
	SO_4	.08	.0152				SO_4	.18	.0001	pH	.21	.0003
							pH	.02	.0695			
Total Ca (rising limb)	Q	.93	.0001	Q	.92	.0001	Q	.90	.0001	Q	.60	.0001
	Col	.02	.0160	Alk	.01	.1653	Col	.03	.0170	SO_4	.31	.0001
	Alk	.02	.0428				SO_4	.02	.0087	pH	.02	.0365
							pH	.01	.0700			
Total Ca (falling limb)	Q	.98	.0001	Q	.86	.0001	Q	.75	.0001	Q	.58	.0001
	SO_4	.01	.0065	Alk	.01	.1251	SO_4	.22	.0001	SO_4	.29	.0024
										Col	.03	.0017
										Alk	.03	.0098

Regression equations for separate limbs of the annual hydrograph (table 2) compare with nonlimb-separation models (table 1) as follows: (1) iron colloid concentration accounted for less of the variation and discharge for more of the variation in the transition metal loads for limb-separation models for site AR05; (2) discharge generally accounted for more of the variation in the transition metal loads for limb-separation models than for nonlimb-separation models at site LD10; (3) iron colloid concentration entered into only the limb-separation models for site CG99; and (4) limbseparation models similar to the composite models applied to the rising and falling limbs of the annual hydrograph at sites AR05, AR65, and LD10. The large p-values in table 2 generally indicated more uncertainty in the limb-separation models, and therefore, this seasonal separation is not warranted for all sites. Increased uncertainty in the limb-separation models might be related to the small sizes of samples.

CONCLUSIONS

Because of the reactive nature of transition metals in streams, estimation of metal loads requires consideration of environmental variables in addition to stream discharge. Among the regression models for total constituent loads of iron, manganese, zinc, and cadmium loads at two main stem sites on the Arkansas River, stream discharge accounts for about one-half of the variability in the constituent load. For total calcium, which is more conservative, stream discharge accounts for more than 90 percent of the variability in the calcium load. Iron- colloid concentration generally accounts for about 26 percent of the variability in the transition metal loads. Combinations of independent variables generally are not transferable from one reach to another on the same stream because of site specific variation. Further analysis of the data and continued monitoring at sampling sites would improve understanding of processes.

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COMPARISON OF RATES OF HYDROLOGIC AND CHEMICAL PROCESSES IN A STREAM AFFECTED BY ACID MINE DRAINAGE

By Briant A. Kimball[1], Robert E. Broshears[2], Kenneth E. Bencala[3], and Diane M. McKnight[2]

ABSTRACT

An instream experiment in St. Kevin Gulch near Leadville, Colorado, in August 1986 examined the interplay between the rate of hydrologic transport and the rates of chemical reactions in affecting streamwater metal concentrations. Lithium chloride was used as a conservative chemical tracer for determining discharge and time of travel along a 1,800-meter reach. With this hydrologic background, a synoptic sampling indicated that reactive and conservative transport of metals occurred downstream from inflows of acidic, metal-rich drainage. There were three basic patterns of mass flow along the reach. Sodium mass flow increased from metal-rich inflows near abandoned mine tailings, and then remained relatively constant. Aluminum and manganese were typically conserved within the stream, with possible mass losses immediately downstream from neutral-pH inflows. Iron was reactive and was removed from the streamwater along the entire reach.

Downstream profiles of metals were simulated using a steady-state equation that accounts for longitudinal advection and additions of lateral inflows. These simulations accounted for the removal of iron by introducing a first-order reaction to the steady-state equation. The rate constant for the net instream removal of iron was found from calibrating the simulation to the observed iron profile. This net rate represents several processes and not a specific reaction. The combination of mass-balance calculations and solute-transport simulations provides insight to the relative importance of hydrologic and nonhydrologic (chemical and biological) processes that affect metal concentrations in acid mine drainage.

INTRODUCTION

Interplay between the rate of hydrologic transport and rates of chemical and biological reactions influences solute concentrations in streamwater. If reaction rates are rapid with respect to transport rates, then concentrations of solutes will be controlled by reactions. On the other hand, if hydrologic transport is more rapid than rates of reactions, then transport will dominate and a solute may be conservative rather than reactive. Rates of nonhydrologic processes in streams are influenced by factors that are difficult to duplicate in laboratory studies.

In St. Kevin Gulch near Leadville, Colo. (fig. 1), metal-rich, acidic inflows that drain abandoned mine tailings add metals that are transported downstream in either a conservative or reactive manner. This paper discusses the results of an instream experiment designed to examine rates of processes downstream from the inflows. Although concentrations of many elements were determined, this paper will focus on the chemistry of Al (aluminum), Fe (iron), Li (lithium), Mn (manganese), and Na (sodium). These metals demonstrate the range of observed transport behavior. Filtered (0.1-micrometer) samples were analyzed for Li by flame atomic-absorption spectroscopy and for the other metals by inductively coupled argon-plasma spectrometry. The details of sampling and analysis have been discussed elsewhere (Kimball and others, 1988; McKnight and others, 1988).

HYDROLOGIC FRAMEWORK FOR CHEMICAL STUDY

In August 1986, a tracer solution of 4.7 moles per liter LiCl (lithium chloride) was injected into St. Kevin Gulch at a rate of 27 milliliters per minute for 52 hours. During the injection, stream discharge was sustained by base flow. Water samples were collected at frequent time intervals at six sites ranging from 26 to 1,804 m (meters) downstream from the site of the LiCl injection (fig. 1). Additional "synoptic" samples were collected along the entire reach for analysis of concentrations of inflows and streamwater above and below inflows (table 1). Several inflows and instream sampling sites are not shown between the sites located in fig. 1 because of the intensive spatial scale of the sampling. All sites are listed in table 1, and sites are referenced throughout by their distance downstream from the LiCl injection.

Physical transport of conservative solutes in a stream is dominated by longitudinal advection, dispersion, lateral inflow, and transient storage. These processes were accounted for in a transient-storage solute-transport simulation model (Bencala and Walters, 1983; Bencala, 1984; Bencala and others, 1990). As input to the transient-storage model, discharge at each frequently sampled site and five synoptic sites was calculated by the dilution required to match the observed plateau concentrations of the tracer. Discharge varied from 6.2 to 19.7 liters per second (table 1). This transient-storage model was used to accommodate deviations from traditional advective-dispersive behavior in the observed concentration profile, defining discharge of laterial inflows, and determining the stream cross-sectional areas necessary for subsequent analysis.

The analysis presented in this paper assumes steady-state conditions. The steady-state profile of a solute undergoing advection, mixing with lateral inflow, and first-order removal may be depicted by the following equation:

$$-Q/A * dC/dx + q_L/A * (C_L - C) - k * C = 0, \qquad (1)$$

where

Q = discharge, cubic meters per second;

A = stream cross-sectional area, square meters;

x = distance, meters;

q_L = lateral inflow rate per unit stream length, cubic meter per second per meter;

C = streamwater solute concentration, milligrams per liter;

C_L = inflow solute concentration, milligrams per liter; and

k = first-order rate constant for net solute removal, inverse seconds.

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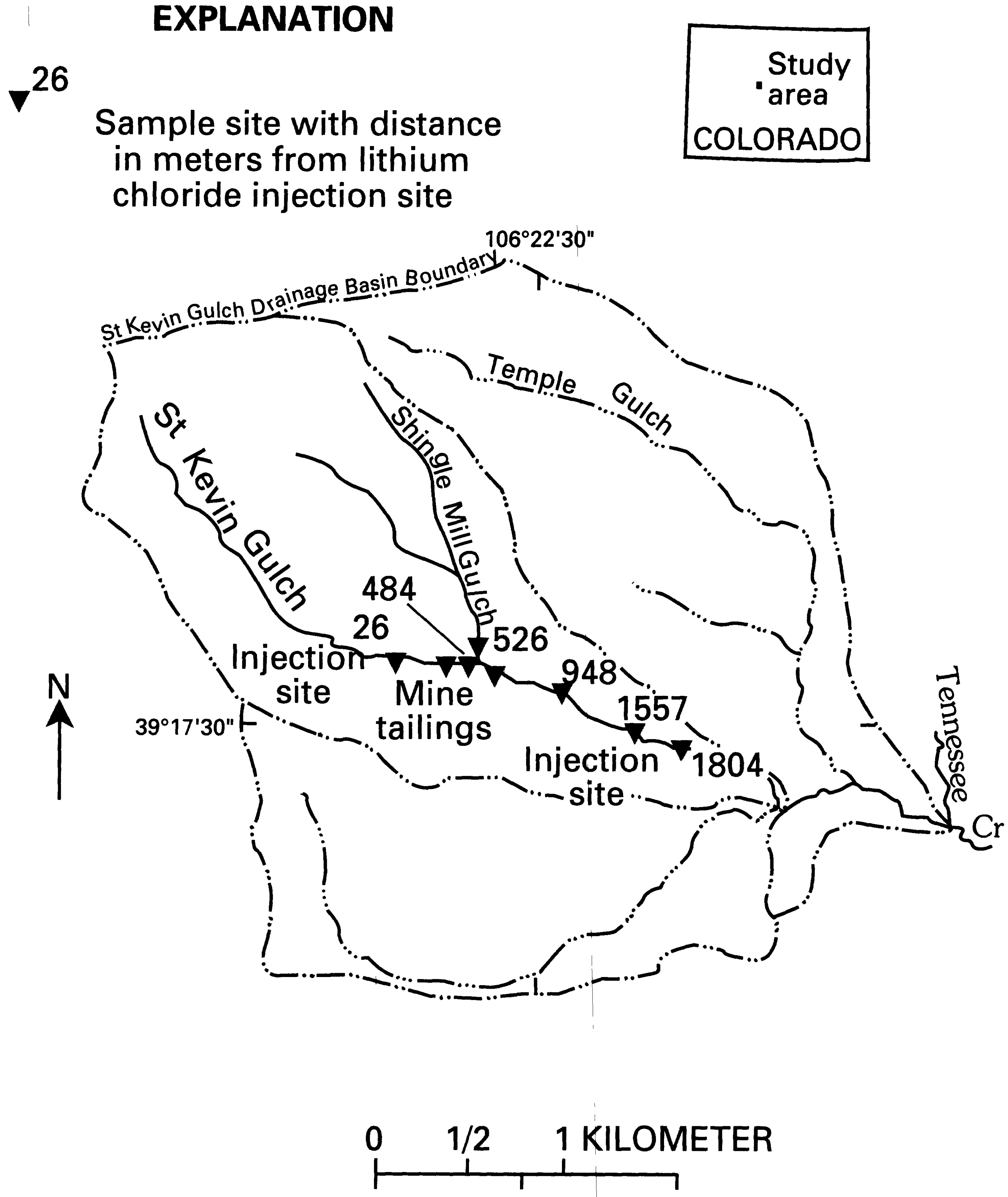
EXPLANATION
▼26
Sample site with distance in meters from lithium chloride injection site
Study area
COLORADO
106°22'30"
St Kevin Gulch Drainage Basin Boundary
Temple Gulch
Shingle Mill Gulch
St Kevin Gulch
484
26
526
Injection site
Mine tailings
948
1557
1804
Injection site
Tennessee Cr
N
39°17'30"
0 1/2 1 KILOMETER
0 1/2 1MILES

Figure 1. Location of study area indicating selected sampling sites.

Table 1. *Summary of synoptic sampling sites*

[Pos, downstream position, in meters; Trib, inflows: 1 = inflow, O = stream; Qss, discharge used in steady-state model, in liters per second; Li, lithium, in milligrams per liter (mg/L); Al, aluminum, in mg/L; Fe, iron, in mg/L; Mn, manganese, in mg/L; Na, sodium, in mg/L]

Pos	Trib	Qss	Li	pH	Al	Fe	Mn	N
26	0	6.19	2.6	4.94	0.806	0.64	2.6	2.1
363	0	6.56	2.0	4.78	1.0	.63	2.0	2.1
372	1	[1] -	.016	2.69	17	61	49	4.9
413	0	6.59	2.2	4.06	1.4	1.5	2.6	2.3
417	1	-	.022	2.66	14	89	56	4.9
418	1	-	.022	2.91	9.1	8.9	16	3.3
421	0	6.78	2.2	3.79	1.6	2.5	3.2	2.3
424	1	-	.021	2.69	14	125	52	5.0
439	0	6.86	2.1	3.61	1.9	5.6	4.9	2.4
449	1	-	.019	2.60	16	123	56	4.8
455	0	7.28	2.0	3.37	2.8	12	7.7	2.4
459	1	-	.019	2.66	16	76	49	4.6
464	0	7.30	2.0	3.29	3.0	12	8.5	2.5
469	1	-	.036	2.72	25	32	37	4.9
484	0	7.92	1.9	3.47	2.7	13	7.9	2.6
501	1	-	.002	6.51	.076	.19	.52	2.0
526	0	15.10	1.1	3.99	.76	5.0	4.3	2.4
586	0	-	.94	3.88	2.1	4.4	4.6	2.4
641	0	-	.98	3.87	2.2	4.2	4.6	2.5
701	0	-	1.0	3.90	2.3	3.9	4.7	2.5
754	0	-	.97	3.85	2.3	3.8	4.6	2.4
781	0	-	.96	3.78	2.3	3.4	4.6	2.6
851	1	-	.08	5.98	.37	.47	.40	2.6
881	0	-	.89	3.91	2.1	2.9	4.4	2.4
948	0	16.80	.76	3.74	1.8	1.4	4.0	2.2
1,068	0	-	.83	3.75	2.0	2.5	4.4	2.4
1,265	0	-	.82	3.69	2.2	1.7	4.3	2.4
1,281	1	-	.03	3.87	1.2	.73	2.8	2.2
1,308	0	-	.75	3.65	2.1	1.8	4.2	2.3
1,391	1	-	.008	6.19	.19	.57	.019	1.4
1,421	0	-	.73	3.59	2.0	1.7	4.1	2.3
1,497	0	-	.71	3.64	2.1	1.6	4.1	2.3
1,557	0	19.70	.70	3.59	2.1	1.3	4.2	2.2
1,677	0	-	.69	3.71	2.0	1.3	4.1	2.3
1,767	0	-	.68	3.65	2.1	1.2	4.1	2.2
1,776	0	-	.70	3.56	2.1	1.4	4.1	2.2
1,804	0	14.70	.74	3.80	2.0	1.4	4.3	2.4

[1] Discharge is assumed to be linear for instream sites between the table values. For inflows, discharge was calculated as the change between the downstream and upstream sites around the inflow.

Equation 1 was solved by a numerical algorithm with physical parameters derived from the transient LiCl simulation. Solute concentrations C and C_L were measured, leaving k as a fitted parameter. The simulated steady-state profile of Li, with no solute removal term (k=0), is shown in figure 2. Conservation of Li is assumed in the estimation of the physical parameters, thus figure 2 verifies consistency between the conservative Li and execution of the model.

GEOCHEMICAL PATTERNS OF METAL TRANSPORT

The reactive or non-reactive behavior of a metal may be indicated by the downstream profile of mass flow, in milligrams per second. Profiles of mass flow rather than concentration account for the loss or gain of mass due to inflows or nonhydrologic processes. Three basic patterns of mass flow were illustrated by solutes in St. Kevin Gulch. The pattern of Na (fig. 3a) entailed an increase in mass flow from inflows that discharge from mine tailings between 373 and 484 m. Downstream from 586 m, the profile of mass flow remained nearly constant. After 1,557 m, the decrease in mass flow is due to an actual loss of water (Zellweger and others, 1991, this Proceedings). This decrease of mass flow also occurs for Al, Fe, and Mn (figs. 3a, 3b, and 3c).

The profiles of Al and Mn (fig. 3b) also showed an increase from inflows near the mine tailings; the mass flow of Mn increases more than Al mass flow. Mn mass flow is very similar to Na mass flow, but the profiles differ because the source of Na is mostly from Shingle Mill Gulch (501 m), and the source of Mn mass flow mostly is from the inflows from the tailings (372, 417, 424, 449, 459, and 469 m). Although the profile of Al mass flow is similar to that of Mn, Al mass flow decreases sharply at 526 m, whereas Mn does not. The Al mass flow increases greatly between 526 and 586 m, but not as much as Mn increases from 363 to 484 m. Between 586 and 1,557 m mass flow of both metals generally increases. Below 1,557 m, the loss of water causes a decrease in mass flow of both metals.

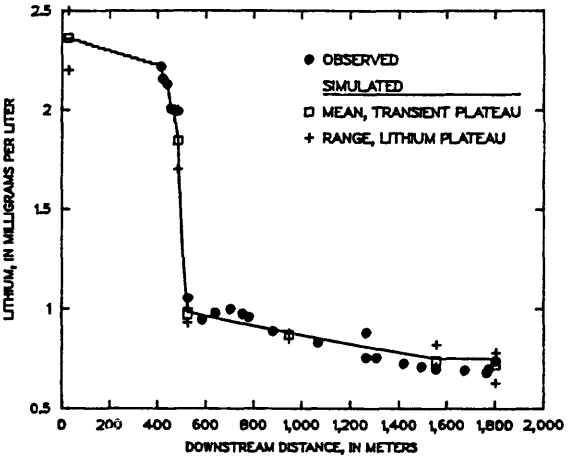

Figure 2. Simulated and observed concentrations of lithium at synoptic sites, August 1986, instream experiment.

The profile of Fe (fig. 3c) showed the same large increase of mass flow from the tailings discharge. Downstream from the maximum Fe mass flow at 484 m, the general pattern indicates a decrease of Fe mass flow all along the reach. This decrease in Fe mass flow is consistent with the ubiquitous hydrous Fe oxides that cover the streambed. The comparison of the mass-flow profiles to the pattern of pH (fig. 3d) indicates that subreaches with losses of Al, Fe, and Mn mass flow received inflows with relatively high pH at 501 and 851 m.

STEADY-STATE SIMULATIONS OF METAL CONCENTRATIONS

Using equation 1 without the solute-reaction term, steady-state profiles of Na, Al, Mn, and Fe were simulated. Measured concentrations of metals in surface inflows were assumed characteristic of inflow concentrations in areas near the inflows. Bencala and McKnight (1987) have discussed inflow concentrations in a similar acidic stream. In general, simulated Al, Mn, and Na concentrations, with no first-order reaction, compare favorably to observed concentrations (fig 4). The most favorable comparison is for Na (fig. 4a). The simulations were less satisfactory for Al and Mn (figs. 4b and 4c). Deviations from observed values were most

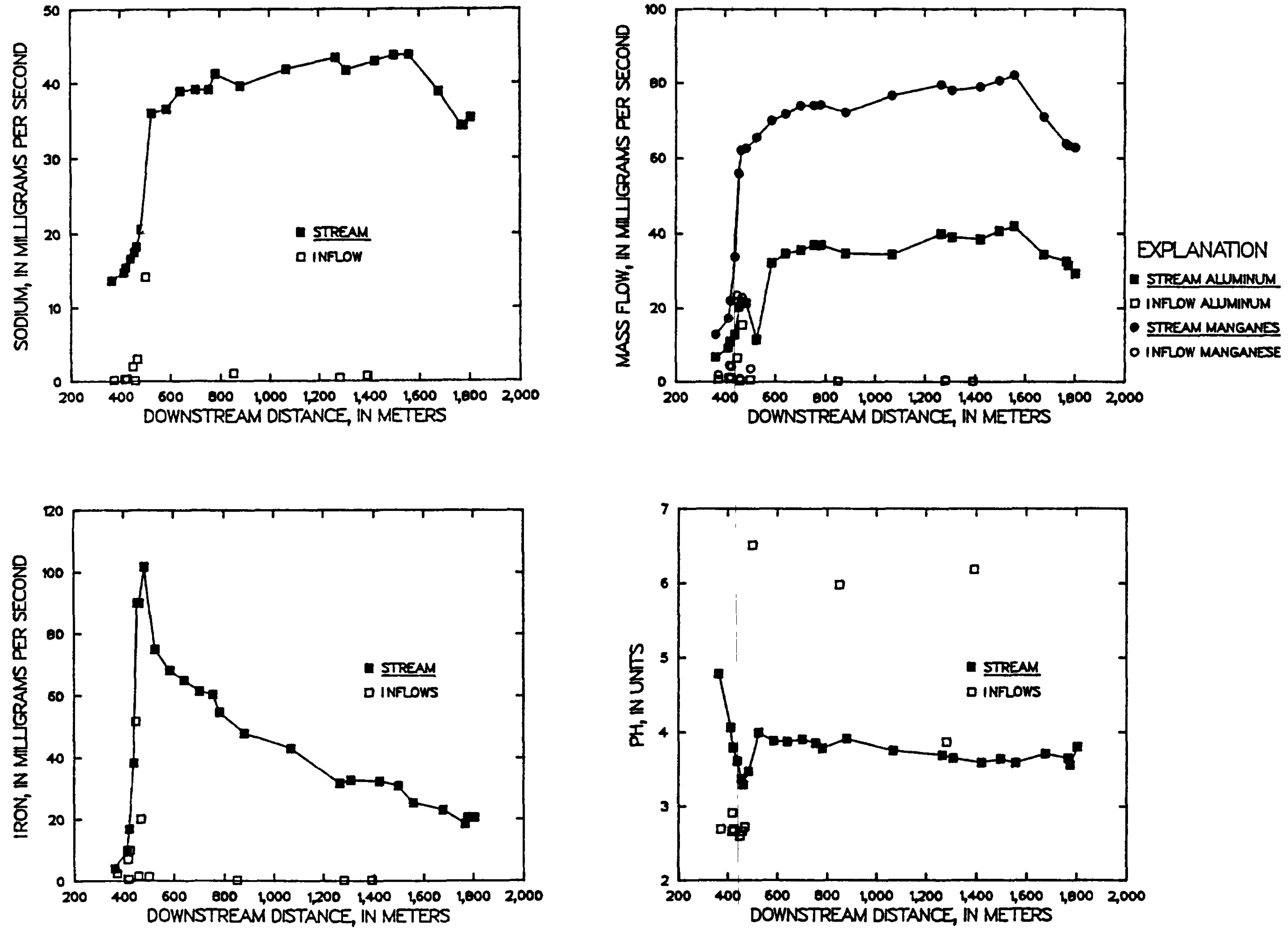

Figure 3. Variation of (a) sodium mass flow, (b) aluminum and manganese mass flow, (c) iron mass flow, and (d) pH with distance downstream from the lithium chloride injection.

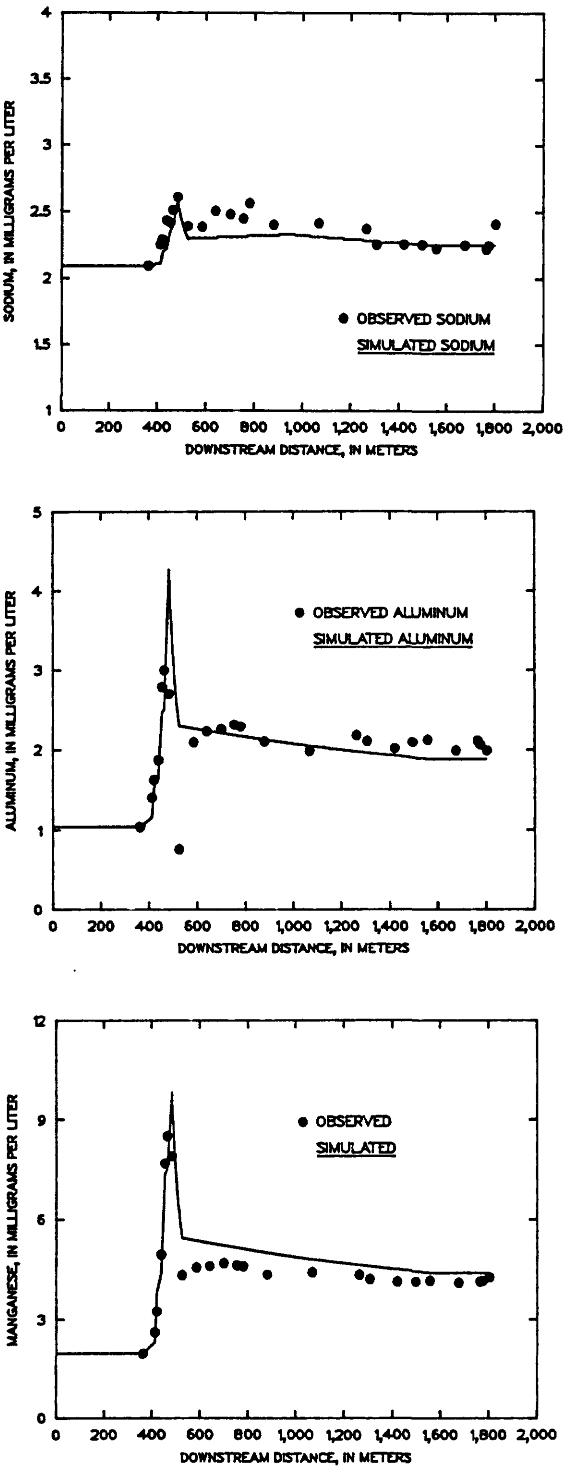

Figure 4. Observed and simulated concentrations of (a) sodium, (b) aluminum, and (c) manganese.

evident in the reach from 484 to 526 m, where the confluence of Shingle Mill Gulch (at 501 m) causes the most abrupt increase of instream pH and again at 948 m, downstream from an inflow (at 851 m) with pH near 6 (fig. 3d). The changes in pH likely are responsible for the nonconservative behavior of these metals and affect Al more than Mn.

Simulated concentrations with no first-order reaction grossly overestimated Fe concentrations downstream from the Shingle Mill confluence (at 501 m; fig. 5). It was possible to simulate the observed Fe concentrations by including a first-order reaction for the net removal of Fe (fig. 5). The appropriate rate constant was found by fitting the simulation to the observed data. The rate of Fe removal appears to be first order in Fe concentration, but it is a pH-dependent process. This net rate represents the combined nonhydrologic processes, both chemical and biological, and is not a specific reaction. A rate constant of 9×10^{-5} s^{-1} was used in the entire simulation except between 484 and 526 m, where a larger value of 7×10^{-4} s^{-1} was needed to fit the data. This is consistent with the instream pH which is probably at its highest values between 501 and 526 m, downstream from Shingle Mill Gulch. Downstream from 526 m, the smaller value of k is sufficient to fit the observed Fe concentrations.

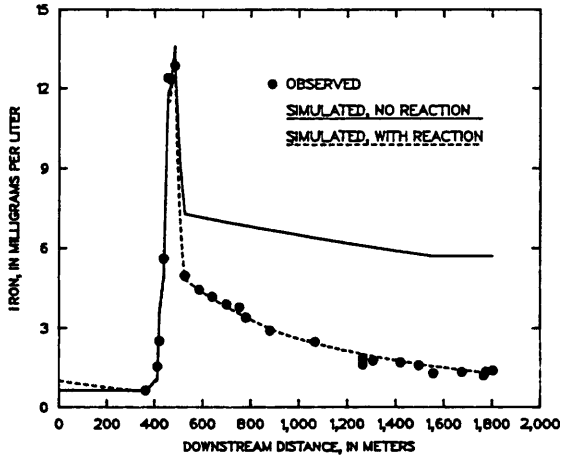

Figure 5. Observed and simulated concentrations of Fe with no first-order reaction and with first-order reaction.

CONCLUSIONS

A mass-flow analysis and solute-transport simulation of data from an instream experiment have identified the relative importance of hydrologic and chemical processes in determining steady-state concentration profiles of metals in a stream affected by acid mine drainage. An analysis of concentration profiles following a LiCl injection defined discharge along an 1,800-m reach of St. Kevin Gulch, near Leadville, Colo. Mass-flow profiles defined three geochemical patterns of metal transport. The profile of Na indicated conservative transport similar to that for Li. Profiles of Al and Mn were consistent with reactive transport downstream from inflows of near-neutral water. The profile of Fe indicated the importance of nonhydrologic processes, such as precipitation and adsorption reactions, through the entire reach. Steady-state simulations show that chemical reactions of Al, Mn, and Fe are sufficiently rapid to affect instream concentrations. The analysis supports the importance of pH as a factor in the chemical reactions. The steady-state simulations complement the analysis of mass-flow profiles, and help determine the interplay between rates of hydrologic and chemical processes.

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PRELIMINARY INVESTIGATION OF THE EFFECT OF HILLSLOPE HYDROLOGY ON THE MECHANICS OF SOLUTE EXCHANGE BETWEEN STREAMS AND SUBSURFACE GRAVEL ZONES

By Judson W. Harvey[1], Kenneth E. Bencala[1], and Gary W. Zellweger[1]

ABSTRACT

The mechanics of solute transport and retention are being investigated in two gravel-bed streams (Little Lost Man Creek, California, and St. Kevin Gulch, Colorado). The overall goal is to determine the influence of hillslope hydrology on solute exchange between the stream channel zone and interstitial water of subsurface gravel zones adjacent to the stream. The first objective of the research was to determine the mechanism responsible for solute exchange between stream and subsurface zones. Solute tracers were released in the stream and in the subsurface, and concentrations were monitored at selected locations to describe transport. Subsurface hydraulic gradients adjacent to the stream were measured simultaneously. Observations indicated that the mechanism of solute exchange was advective exchange between the stream and ground water of the adjacent gravel zone. The stream tracer (chloride) moved away from the stream and entered the subsurface zone where the subsurface hydraulic gradient was away from the stream. The subsurface tracer (bromide) moved toward the stream where the gradient was toward the stream.

The second objective of the research was to examine hydrological controls on advective solute exchange with the subsurface. The magnitude of subsurface hydraulic gradients was observed to vary on a diel cycle. Where the gradient was away from the stream, advection away from the stream increased during the day and decreased at night. Conversely, where the gradient was toward the stream, advection toward the stream decreased during the day and increased at night. As a result, there was more loss of streamwater to the adjacent subsurface during the day than at night.

Several possible mechanisms were considered to explain the diel variation in subsurface hydraulic gradients and advection perpendicular to the stream. Evapotranspirative pumping of subsurface water out of the gravel and soil zone at the base of the hillslope was the explanation most consistent with observations. These preliminary findings suggest that hillslope hydrology has important effects on the direction and magnitude of water and solute exchange between streams and subsurface zones. Further investigations of hillslope-stream interactions and effects on solute transport are warranted.

INTRODUCTION

Highly porous gravel and sand deposits are present beneath and adjacent to gravel-bed streams. Solutes in streamwater have been shown to be transported into subsurface zones, stored there for a period of time, and then transported back into the stream. This exchange of solute between the open channel and the subsurface is well documented in a few gravel-bed streams (Bencala, 1984; Kennedy and others, 1984; Cerling and others, 1990). The interaction between the stream and these subsurface zones has been shown to delay the downstream arrival of solute released in the stream, increase the contact time of streamwater with sediment, and affect chemical reaction (Aumen and others, 1990).

The mechanisms that could drive solute exchange between streams and subsurface zones are well known in principle, but specific controls on solute exchange between streams and subsurface zones are poorly understood. Solute exchange between streams and the subsurface have been modeled most successfully on a purely empirical basis (Bencala and Walters, 1983; Jackman and others, 1984, Aumen and others, 1990). An improved understanding of the mechanisms and controls involved in subsurface storage of solutes is crucial to understanding the link between hydrological retention, chemical mass balance and chemical reaction in stream ecosystems.

The overall purpose of this study is to determine the effect of hillslope hydrology on solute exchange between stream and gravel subsurface zones. The specific objectives of the research described herein were to determine (1) whether significant advective exchange of streamwater (and solute) occurs between the stream and subsurface zones at St. Kevin Gulch, and (2) whether spatial and temporal variation in that exchange occurs as the result of hydrological processes on the hillslope.

METHODS

Field studies have begun in two gravel-bed streams--Little Lost Man Creek in Humboldt County, Calif., and St. Kevin Gulch in Lake County, Colo. At St. Kevin Gulch, a representative section of stream, and an adjacent area on the lower hillslope were selected for experimentation (fig. 1a). A total of 19 cased wells (5 cm (centimeters) inside diameter) were installed and 6 shallow sampling pits were dug in the sediments of the lower hillslope at St. Kevin Gulch. The wells were distributed within a closely spaced array, extending over an 8 x 4 m (meter) area. Chloride was injected (at a constant rate and concentration) for 4 days, beginning August 20, 1990, in St. Kevin Gulch at a distance 77 m upstream from the well array. Beginning 1 day later (August 21), an additional conservative tracer, bromide, was injected continuously for a 3-day period into a well located 2 m away from the stream, and upstream from most wells in the array (fig. 1b). The instream injection and subsequent stream sampling followed the procedures of Kennedy and others (1984), and well injections and well sampling followed the general methods of Triska and others (1989).

Hydraulic heads were measured periodically in wells using a graduated rod fitted with electrical wires to sense a change in resistance when contact was made with the water surface. Distances were measured from the top of the well casings (or tops of staffs in pits or the stream) down to the

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[1] U.S. Geological Survey, Menlo Park, Calif.

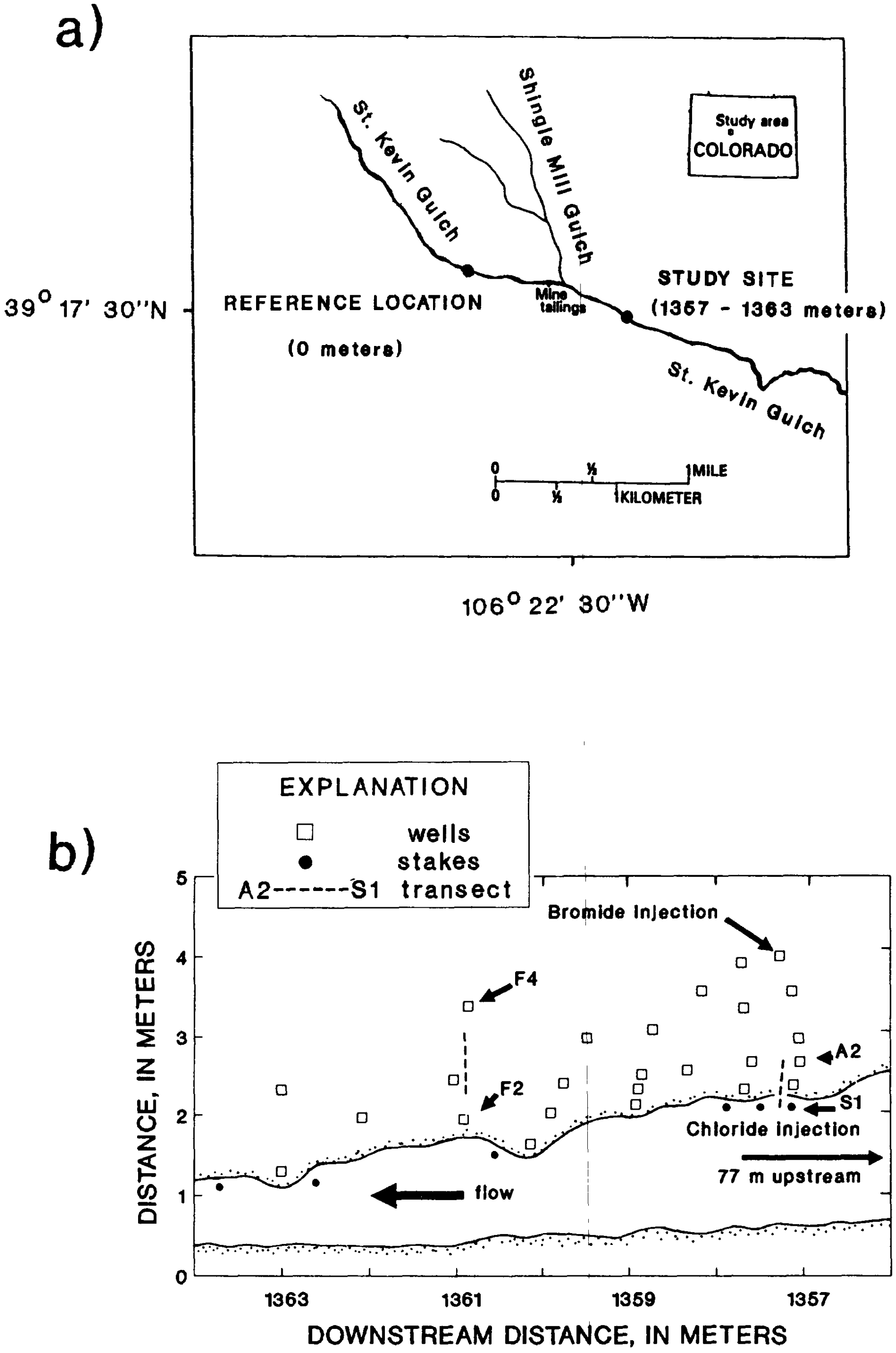
a)
St. Kevin Gulch
Shingle Mill Gulch
Study area
COLORADO
STUDY SITE
(1357 - 1363 meters)
REFERENCE LOCATION
(0 meters)
Mine tailings
St. Kevin Gulch
0 ½ 1 MILE
0 ½ 1 KILOMETER
39° 17' 30"N
106° 22' 30"W
b)
EXPLANATION
□ wells
● stakes
A2------S1 transect
Bromide Injection
F4
F2
A2
S1
Chloride Injection
77 m upstream
flow
DISTANCE, IN METERS
0
1
2
3
4
5
1363
1361
1359
1357
DOWNSTREAM DISTANCE, IN METERS

Figure 1. Study area: (a) general location of St. Kevin Gulch and site of hillslope influence experiment, (b) distribution of wells and location of tracer injections. Distances downstream are referenced to a common reference used in St. Kevin Gulch for work related to the Toxic Substances Hydrology Program, USGS (B.A. Kimball, U.S. Geological Survey, oral commun., 1990.)

phreatic surface. Those measurements were related to a common baseline using surveyed elevations of well tops or staff tops. The bias in measuring hydraulic head (sum of accuracy and precision) was estimated to approximately 0.25 cm. Horizontal hydraulic gradients perpendicular to the stream were estimated along two subsurface transects perpendicular to streamflow. Transect [a] was from well A2 to location S1 at the edge of the stream. Transect [b] was from well F4 to well F2 (fig. 1b). Hydraulic gradients were computed as the difference in hydraulic head between endpoints on the transect, divided by the horizontal length of the transect. Hydraulic gradients computed for a phreatic surface that sloped toward the stream were assigned as positive; gradients for a phreatic surface that sloped away from the stream were therefore negative. Stream discharge was measured using a Parshall flume with a 3-inch throat. Tracer samples were returned to the laboratory following conclusion of the experiment, and chloride and bromide concentrations were analyzed by ion chromatography.

RESULTS

Over a period of 4 days, conservative solute tracers were exchanged between the stream and adjacent subsurface zone over distances exceeding 2 m (perpendicular to the stream). A contour map showing the distribution of chloride concentrations on August 24 (4 days after the start of the chloride injection) indicates that chloride entered the subsurface at the upstream end of the array (fig. 2a). On August 27, 3 days after the chloride injection ceased, chloride was detectable at only very low concentrations in the stream channel (0.4 mg/L (milligrams per liter)) but was still present at high concentration in the subsurface (> 6 mg/L). A contour map of chloride concentrations on August 27 shows that a plume of chloride-labeled water had moved farther into the subsurface zone at the upstream end of the well network, parallel to the stream in the midsection of the well network, and back toward the stream at the downstream end of the network (fig. 2b). Over a 6-day period, the subsurface tracer (bromide) moved parallel to the stream at the upstream end of the array and toward the stream at the downstream end of the well network (fig. 2c).

Water flows from locations of higher hydraulic head to locations of lower head. For this study, subsurface flow lines are assumed to be horizontal and perpendicular to contours of hydraulic head. A contour plot of hydraulic head in the well network at St. Kevin Gulch provides a view of the hydraulic potential field that drives horizontal convection in the subsurface. Flow from the stream to the subsurface can be inferred to have occurred in the upstream half of the network and flow from the substream back into the stream can be inferred to have occurred in the downstream half of the network (fig. 3a).

The subsurface hydraulic gradient perpendicular to streamflow was negative (away from the stream) on transect [a], in the same zone where chloride was transported away from the stream and into the subsurface. On transect [b] the hydraulic gradient was positive (toward the stream), in the area where bromide was transported toward the stream (figs. 2 and 3).

Diel variation in the magnitude of the hydraulic gradients is apparent. On both transects the gradients decreased during the day and increased at night (figs. 3a and 3b). On transect [a], where the gradient was always negative (transport was away the stream), this diel variation meant that the rate of streamwater advection into the subsurface was greatest during the day and least at night. On transect [b], where water and solute were transported toward the stream, the rate of convection into the stream decreased during the day and increased at night (figs. 3a and 3c).

The diel variation that was evident in hydraulic gradients was also present in stream discharge. Minimum and maximum values of discharge occurred at about the same time or slightly after minima and maxima in the fluctuating hydraulic gradients (figs. 3b and 3c).

DISCUSSION

Over an 8-m reach of stream at St. Kevin Gulch, advection occurred out of the stream in the upstream half of the reach, and from the subsurface back into the stream in the downstream half. The flow path was defined using tracers and substantiated by measurement of subsurface hydraulic gradients. The process of advective transfer of solutes from stream to the subsurface zone, and then back into the stream at downstream locations after mixing with subsurface water, was hypothesized by Kennedy and others (1984) as a mechanism to explain changes in concentration of a stream tracer in Uvas Creek, Calif. The data presented in this paper support the conclusion of Kennedy and others (1984) that exchange occurs by advection, and that advection occurs in both directions (subsurface into the stream and stream into the subsurface).

Time-dependent measurements showed that the hydraulic gradient toward the stream fluctuated on a diel basis. The hydraulic gradient toward the stream decreased during the day and decreased at night. The timing of the decrease in discharge in the stream was similar to the timing of (1) increased water loss from the stream into the subsurface at streamside locations with negative hydraulic gradients (for example, transect [a]), and (2) decreased input of water to the stream at streamside locations with positive subsurface hydraulic gradients (for example, transect [b]). At night, the gain in stream discharge was related to converse conditions in the subsurface, that is, water flow from the stream to the subsurface decreased at night (transect [a], fig. 3b), and flow from the subsurface to the stream increased at night (transect [b], fig.3c).

The net result of above fluctuations was that streamwater was drawn into the substream zone during the day, mixed with subsurface water, and then a mixture of water was released back into the stream at night. The fluctuations in stream discharge that accompany the observations of hydraulic gradients have been observed in a number of low-flow streams. Other investigators contended that the discharge variation was caused by hillslope processes; their interpretation was that diel variation in ground water inflow to the stream channel may have resulted from evapotranspiration on the lower hillslope (Bencala and others, 1984; Kobayashi and others, 1990). In the present study, measurements of subsurface hydraulic gradients provided evidence consistent with that interpretation.

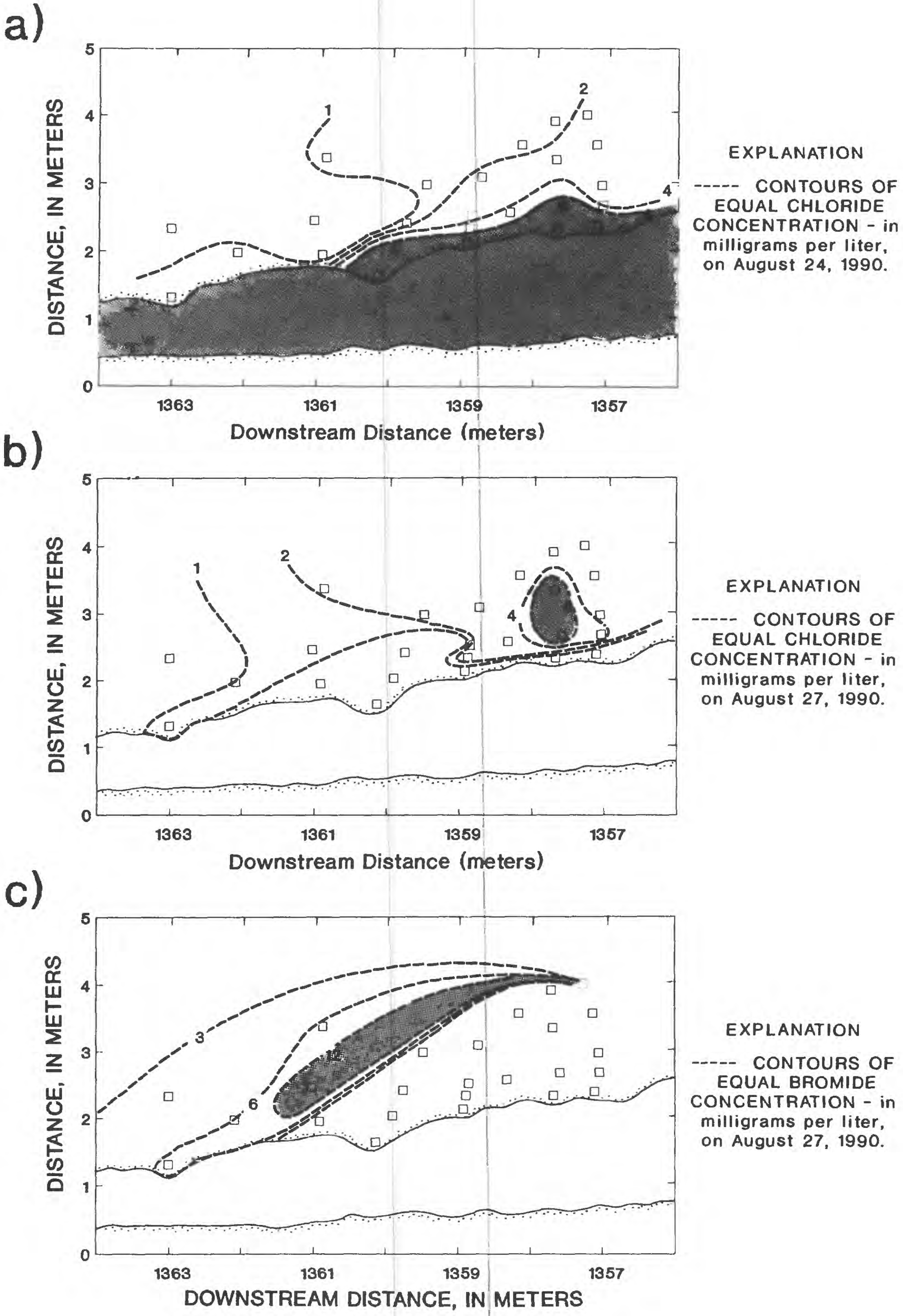

Figure 2. Tracer concentrations at the St. Kevin Gulch study site. Zones of highest concentration (> 6 mg/L for chloride and > 12 mg/L for bormide) are shaded. (a) Chloride on August 24, (b) chloride on August 27, (c) bromide on August 27.

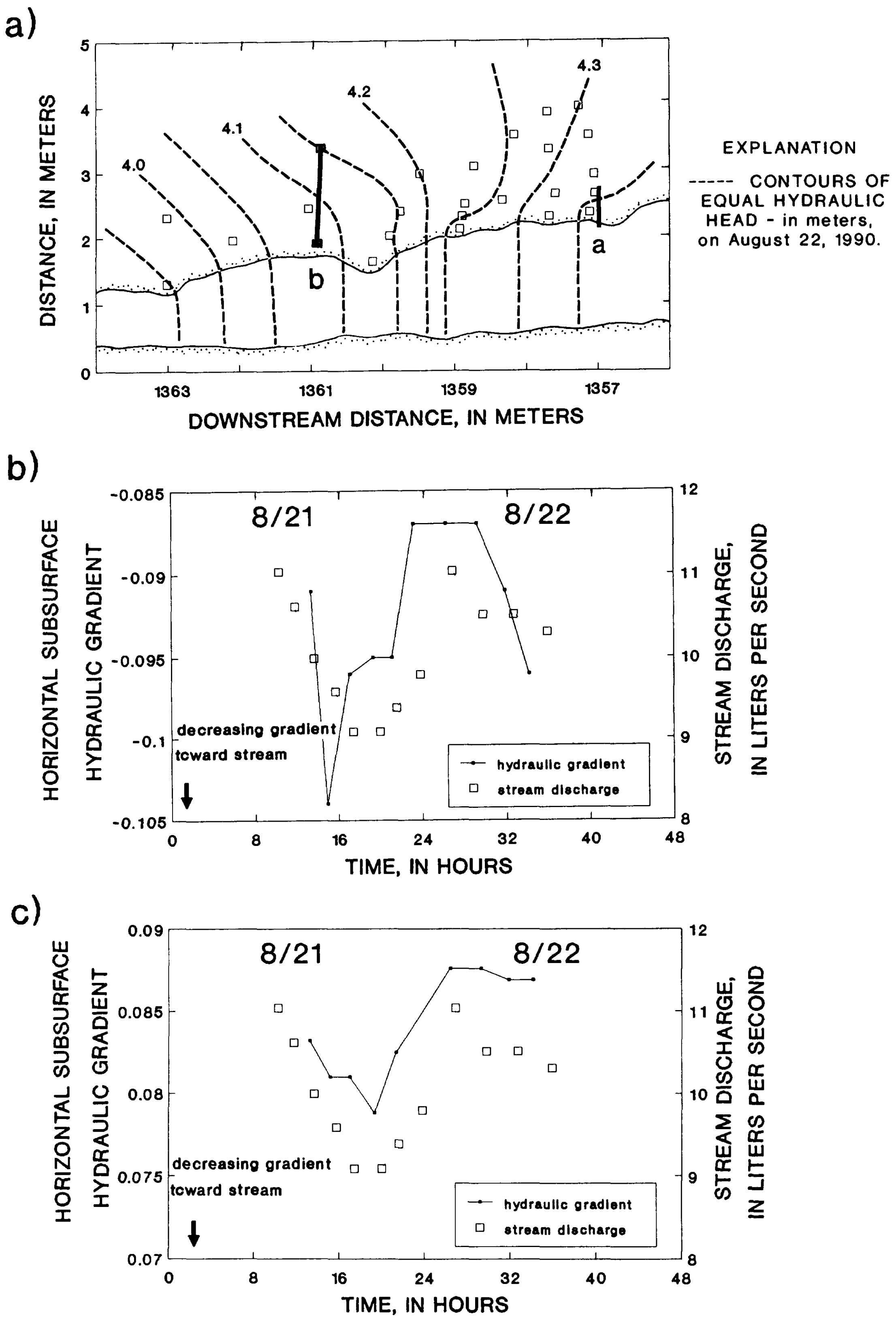

Figure 3. Spatial and temporal patterns in hydraulic head and in hydraulic gradients at the St. Kevin Gulch study site. (a) Contours of hydraulic head in meters (above an arbitrary datum), (b) temporal change in the subsurface hydraulic gradient on transect [a] and in stream discharge, (c) temporal change in the subsurface hydraulic gradient on transect [b].

Discharge variation in the stream appeared to follow and result from changes in the subsurface hydraulic gradient toward the stream (figs 3b and 3c).

Factors other than evapotranspiration could affect subsurface hydraulic gradients and stream discharge at St. Kevin Gulch. For example, unsteady delivery of streamwater from an upstream source (for example, isolated snow patch) could affect streamflow and subsurface hydraulic gradients, but a source of water from upstream would lead to a decrease in the local subsurface hydraulic gradient upon arrival of the streamwater pulse in the study area. Instead, an increase in the local subsurface hydraulic gradient was observed at times of highest discharge (figs. 3b and 3c). Also, a downstream lag in the time of the minimum discharge would be expected given an upstream point source for the discharge fluctuation, but simultaneous observations of discharge from different locations on Colorado mountain streams do not exhibit such a lag under dry, late summer conditions (McKnight and Bencala, 1990; G.W., Zellweger, U.S.Geological Survey, oral commun., 1990).

Changes in the viscosity of streamwater (coincident with changes in temperature of streamwater) might also affect stream-substream exchanges by affecting the hydraulic conductivity of the sediment (Jaynes, 1990). Although the measured fluctuation in the stream temperature at St. Kevin Gulch was as much as 7 °C (degrees Celsius), the temperature fluctuation in the subsurface water (20 cm from the stream) was less than 0.5 °C, which makes temperature effects an unlikely explanation for diel fluctuations in hydraulic gradients and discharge at this site. However, the pattern of fluctuations in the subsurface hydraulic gradient, as well as the warm, dry, sunny weather at the field site in August, are consistent with an interpretation that fluctuations were a response to evapotranspiration on the lower hillslope.

Future work on hillslope-stream interactions will be directed both at (1) expanding the field measurement program to include larger spatial scales and longer time scales of inquiry and (2) examining the physics of hillslope-stream interactions and the plausibility of interpretations of field data using numerical hydrological models.

SUMMARY

The data from St. Kevin Gulch presented in this paper demonstrate that (1) exchange of water and solute occurs between stream and subsurface zones by advection and, (2) the rate and direction (stream to subsurface or subsurface to stream) of exchange at a location in the stream depend upon changes in the local, horizontal subsurface hydaulic gradient. These data support a preliminary conclusion that hillslope hydrology has a significant effect upon the rate of solute exchange between the stream channel and the adjacent substream zone. Data collected on the diel time scale indicated that some water in the stream channel is alternately drawn into the subsurface, mixed with subsurface water and then a mixture of waters is released back into the stream. Further studies of hillslope-stream interactions are needed on longer time scales and larger spatial scales. Such studies will be important to improving our understanding of the role of hillslope hydrology in chemical transport and reactions in streams.

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CHEMICAL COMPOSITION OF THE WETLAND VEGETATION RECEIVING THE ACID MINE-DRAINAGE WATERS OF ST. KEVIN GULCH, LEADVILLE, COLORADO

By B.M., Erickson[1], P.H. Briggs[1], K.R. Kennedy[1], *and* T.R. Peacock[1]

ABSTRACT

Samples of two species of Carex (sedge) were collected from two ecosystems throughout the St. Kevin Gulch wetland, Leadville, Colorado, to evaluate the effect of these acid mine-drainage waters on the vegetation. Summary statistics indicate very little difference between the chemical composition of the two species. The greatest percentage of variance for most elements in one of the species appears to be related to the geographical difference between the 122-meter-square sampling sites and the 30.5-meter-square sampling sites. Clusters of elevated concentrations for 13 elements in the sedge samples were found at the area of first contact with the wetland, indicating that the vegetation has been affected. Clusters of elevated concentrations in other areas of the wetland demonstrated that water from St. Kevin Gulch is not the only source of contamination to the wetland.

INTRODUCTION

In 1988 a study of the vegetation on the 26-hectare wetland receiving acid mine drainage from St. Kevin Gulch, Leadville, Colo., was initiated (fig. 1). The wetland is a sedge meadow with two major ecosystem components. The aquatic component is dominated by *Carex utriculata* Boott. (Sedge A), and the drier hummock component by *Carex canescens* L. (Sedge B). Samples of sedges from both components were collected throughout the wetland. This paper describes the baseline element concentrations in both species of sedge, results of analysis of variance (ANOV) for Sedge A, and the elements being transferred from the St. Kevin Gulch water to the wetland vegetation.

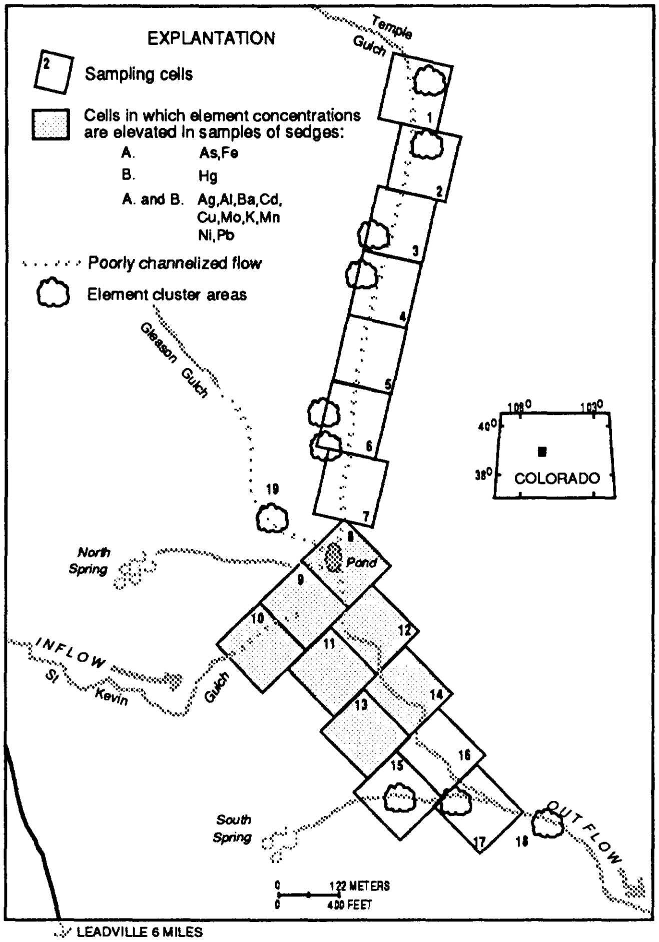

Figure 1. Location of sampling cells on wetland receiving acid mine-drainage waters from St. Kevin Gulch, Leadville, Colorado.

Study Procedures

The wetland was divided into 19 cells, 122 m (meters) on a side, for an unbalanced ANOV sampling design. Each cell was divided into four sections (61 m on a side), three of the four sections were chosen randomly, and three sample sites established to represent the 61-m-square level. The remaining section was then divided again into four 30.5-m-square sections, and two sections were chosen randomly for sampling sites. To evaluate site variance, one of the five sampling sites within each of the 19 cells was randomly chosen, and a duplicate sample was collected. The number of possible samples per cell was 6 and 114 for the wetland.

Samples of Sedge A and Sedge B were collected at each sampling site throughout the wetland wherever possible. Each sample was a composite collected within a 5-m area close to each designated sampling site. The above-ground part needed to fill a 12-cm (centimeter) by 18-cm cloth sampling bag was clipped with stainless-steel clippers. Some sites had been heavily grazed by cattle, limiting the amount of sedge that could be collected. Samples of Sedge A were collected at 94 sites and of Sedge B at 92 sites.

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. The samples were then pulverized and a small split of the raw material saved for atomic absorption analyses. Splits of the samples were also made for estimates of variance caused by preparation techniques and (or) analytical precision. The 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.

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[1] U.S. Geological Survey, Denver, Colo.

Chemical analyses were performed by a 40-element inductively coupled plasma-atomic emission spectroscopy (ICP-AES) method developed by Crock and others (1983). Arsenic (As) was determined by continuous-flow, hydride-generation atomic absorption spectroscopy (HGAAS) (Crock and Lichte, 1982), and mercury (Hg) by cold-vapor atomic absorption (Kennedy and Crock, 1987).

Before statistical processing, elements were eliminated if more than one-third of their data were below the limit of detection, with the exception of silver (Ag) and cadmium (Cd). Ag concentrations are known to be elevated in the St. Kevin Gulch waters, and Cd is an environmentally important element. The qualified values in the remaining data set were replaced with a real value equal to 0.7 times the lower limit of detection according to methods described by Miesch (1976). Elements reported on ash-weight basis (ICP analysis) were converted to dry-weight equivalents, and all data were converted to logarithms prior to statistical analysis. Statistical analysis of the data was performed using the U.S. Geological Survey's STATPAC library of statistical programs (VanTrump and Miesch, 1977).

RESULTS

Summary statistics for both sedges are reported as the geometric mean (GM), geometric deviation (GD), and baseline or expected range (GM/GD^2 - $GM.GD^2$) for 21 elements and the ash content in tables 1 and 2. Visually comparing the results on the two tables, there appears to be very little difference between the element concentrations of Sedge A and Sedge B. Factor analysis of the data is pending.

Table 1. *Summary statistics for element concentrations in Sedge A (Carex utriculata, collected off of the hummocks) Leadville, Colorado, wetland*

[Concentrations are in mg/kg (milligrams per kilogram), dry-matter basis, except ash yield and potassium which are in g/cg (grams per centigram)]

Element	Detection ratio	Geometric mean	Geometric deviation	Baseline or expected range
Ash	94:94	7.60	1.47	3.5 - 16.4
Ag	25:94	.28	1.78	.09 - .89
Al	94:94	50	1.74	17 - 151
As	77:94	.12	2.23	.02 - .60
Ba	94:94	9	1.61	3.5 - 23
Ca	94:94	3,200	1.36	1,730 - 5,919
Cd	38:94	.34	1.98	.09 - 1.3
Co	44:94	.15	1.57	.06 - .37
Cr	92:94	.34	1.60	.13 - .87
Cu	94:94	6.20	1.70	2.1 - 17.9
Fe	94:94	270	1.86	78 - 934
Hg	44:94	.02	1.64	.007 - .05
K	94:94	1.70	1.18	1.2 - 2.4
Mg	94:94	1,800	1.40	918 - 3,528
Mn	94:94	317	1.65	116 - 863
Mo	58:94	.45	2.14	.10 - 2.1
Na	94:94	30	1.63	11 - 80
Ni	86:94	.86	2.04	.21 - 3.6
P	94:94	2,200	1.14	1,693 - 2,859
Pb	58:94	.96	2.40	.17 - 5.5
Sr	94:94	13	1.45	6 - 27
Zn	94:94	166	2.28	32 - 863

Table 2. *Summary statistics for element concentrations in Sedge B (Carex canescens collected on the hummocks), Leadville, Colorado, wetland*

[Concentrations are in mg/kg (milligrams per kilogram), dry-matter basis, except ash yield and potassium which are in g/cg (grams per centigram)]

Element	Detection ratio	Geometric mean	Geometric deviation	Baseline or expected range
Ash	92:92	7	1.18	5 - 9.7
Ag	24:92	.27	1.86	.08 - .93
Al	92:92	55	1.74	18 - 167
As	66:92	.09	2.32	.02 - .48
Ba	92:92	9	1.54	3.8 - 21
Ca	92:92	3,247	1.34	1,808 - 5,830
Cd	44:92	.33	2.07	.08 - 1.4
Co	58:92	.16	1.67	.06 - .45
Cr	92:92	.34	1.64	.13 - 91
Cu	92:92	6	1.57	2.4 - 14.8
Fe	92:92	229	1.82	69 - 759
Hg	52:92	.02	1.78	.006 - 06
K	92:92	1.40	1.22	.94 - 2.1
Mg	92:92	1,628	1.49	733 - 3,614
Mn	92:92	354	1.61	137 - 918
Mo	67:92	.39	1.92	.11 - 1.4
Na	92:92	22	1.60	8.6 - 56
Ni	89:92	.89	1.98	.23 - 3.5
P	92:92	1,976	1.15	1,494 - 2,613
Pb	62:92	.92	2.31	.17 - 4.9
Sr	92:92	12	1.48	5.5 - 26
Zn	92:92	170	2.11	38 - 757

The detailed use of an unbalanced ANOV design for biogeochemical studies is given by Erdman and Gough (1977). In the present study, five levels for the ANOV were used. The design allows estimation of how the element concentration is affected by geographic location (122-m-, 61-m-, and 30.5-m-square levels), field sampling technique, and preparation techniques and (or) analytical precision. Results of the ANOV for 19 elements and ash content in Sedge A (table 3) indicate that a significant amount of

Table 3. *Distribution of element concentration variation in Sedge A collected on the Leadville, Colorado, wetland*

[* indicates variance component tested significant at the 0.05 probability level; Ag and Cd not included as more than one-third of their data were qualified]

	Variance Among			
Element or ash yield	122-meter-square cells	61-meter-square cells	30.5-meter-square cells	Field duplicates
Ash	*36.63	1.83	*46.36	8.97
Al	*52.56	18.04	*23.12	* 4.47
As	*19.93	2.91	*64.36	5.14
Ba	*40.75	0	*39.07	0
Ca	*14.12	19.75	*42.22	*22.23
Co	*24.07	0	*49.46	3.08
Cr	*52.80	0	18.02	18.65
Cu	*44.99	11.54	*40.98	* 2.13
Fe	6.99	*67.25	5.71	*18.95
Hg	*32.79	0	*38.88	13.02
K	*13.32	26.80	*40.26	3.34
Mg	*67.08	5.76	8.70	*14.99
Mn	*23.49	0	*62.55	*13.83
Mo	*25.10	0	*56.66	*17.91
Na	*17.22	*54.73	* 2.31	24.84
Ni	*22.81	0	*71.19	* 5.24
P	*29.33	*35.55	0	19.18
Pb	*21.88	*43.29	*34.06	0
Sr	1.61	35.19	36.05	*25.44
Zn	*42.91	*39.71	*16.60	*.71

variation in all elements, except strontium (Sr) and iron (Fe), can be explained as the difference between the 19 cells (122-m-square level). Elements with significant differences related to the 61-m-square level are Fe, sodium (Na), phosphorus (P), lead (Pb), and zinc (Zn). In addition, a significant amount of the variancy for all elements except chromium (Cr), Fe, magnesium (Mg), P, and Sr can be explained as the difference between the 30.5-m-square sampling sites. Elements with a significant amount of their variance explained by how the samples were collected in the field are aluminum (Al), calcium (Ca), copper (Cu), Fe, Mg, manganese (Mn), molybdenum (Mo), Na, nickel (Ni), Sr, and Zn. Preparation technique and analytical precision variance percents were all less than 30 percent and not considered significant. Results for the ANOV of Sedge B are not presented in this paper. Only four samples were large enough to split for the fifth level. Further analysis of Sedge B data is pending.

All data for both sedges were plotted on individual base maps and areas where element concentrations exceeded the GM (tables 1 and 2) identified. If the wetland vegetation has been affected by the waters of St. Kevin Gulch, elevated element concentrations would be expected to cluster in the area of direct contact with the water. St. Kevin flows to the east from the mountains, turns north into the wetland and spreads out in the areas of cells 9, 10, 8, 11, 12, 13, and 14 (fig. 1). Elevated concentrations for Ag, Al, barium (Ba), Cd, Cu, Mn, Mo, Ni, Pb, and Zn in Sedge A and Sedge B clustered in this area. Elevated concentrations for As and Fe in samples of Sedge A and Hg in samples of Sedge B also cluster in this area.

The inflow area for St. Kevin was not the only area identified where clusters of elevated element concentrations are present in the vegetation. Clusters also were found in cells at the north end of the wetland (1 and 2), and in cells 3 and 4, cells 6 and 7 in the middle, cell 19, cells 15 and 17 at the southern end, and at the outflow area or cell 18 (fig. 1). Sources of surface water to the wetland (Temple Gulch, Gleason Gulch, North Spring, and South Spring) probably account for all of the additional clusters except for the areas in cells 3 and 4 and cells 6 and 7. Ground-water input and (or) elevated concentrations of metals in the substrate may explain the element clusters in these areas.

SUMMARY

The summary statistics indicate there is very little difference between the chemical content of Sedge A and Sedge B, and the ANOV results suggest that most significant variances in element concentrations in Sedge A are related to the geographical differences existing between the 122-m- and 30.5-m-square sampling sites. The elevated element clusters at the inflow area illustrate that the wetland vegetation has been affected by the acid mine-drainage waters of St. Kevin Gulch. Clusters of elevated element concentrations in other areas of the wetland indicate that St. Kevin Gulch is not the only source of contamination. All but two of the areas with elevated concentrations can be related to surface-water input to the wetland. The remaining two areas are probably related to the effects of ground water or to elevated concentrations of metals in the substrate.

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EFFECT OF ORGANIC MATTER COPRECIPITATION AND SORPTION WITH HYDROUS IRON OXIDES ON ELECTROPHORETIC MOBILITY OF PARTICLES IN ACID MINE DRAINAGE

By James F. Ranville[1,2], Kathleen S. Smith[1,2], Diane M. McKnight[1], Donald L. Macalady[2], *and* Terry F. Rees[3]

ABSTRACT

St. Kevin Gulch is a small, acidic (pH <4.5) subalpine stream located near Leadville, Colorado. Hydrous iron oxides are dominant minerals in this system. This paper investigates the role of organic matter in controlling the surface charge of hydrous iron oxides formed in St. Kevin Gulch and in laboratory experiments designed to simulate the stream. The electrophoretic mobility of the iron-rich suspended sediments is strongly related to their organic carbon content and the dissolved organic-carbon concentration of the streamwater. Organic-carbon concentration is high (10-24 percent) in the suspended sediments. Concentrations of organic carbon in the suspended sediments and dissolved organic carbon in the streamwater become elevated during spring runoff coincident with the presence of negatively charged suspended sediments. Particles are positively charged during midsummer when concentrations of dissolved organic carbon and organic carbon in the suspended sediments are lowest. This is likely the result of an insufficiency of organic matter needed to coat completely the abundant hydrous iron oxides surfaces formed at that time. Organic matter is associated with the suspended sediments as a result of sorption and coprecipitation with hydrous iron oxides. Laboratory experiments with synthetic hydrous iron oxides and Suwannee River fulvic acid indicate coprecipitation removes greater amounts of organic matter than does sorption. However, coprecipitated organic matter has less effect on electrophoretic mobility than does sorbed organic matter. Experiments with Suwannee River fulvic acid, Shingle Mill Gulch fulvic acid, and Shingle Mill Gulch whole organic matter, indicated Suwannee River fulvic acid had a much greater effect on electrophoretic mobility than either of the Shingle Mill Gulch organic matters, possibly because of differences between the environments from which these samples were isolated.

INTRODUCTION

St. Kevin Gulch is a small, acidic (pH <4.5) subalpine stream located approximately 7 km (kilometers) northwest of Leadville, Colo. Hydrous iron oxides (HIO) are dominant minerals in this system as they are in most streams affected by acid mine drainage. These minerals can control aqueous concentrations of various metals through adsorption-precipitation reactions, which, in turn, can depend on the chemical and electrical properties of HIO surfaces. The net charge on HIO surfaces is pH-dependent because of the amphoteric nature of the surface hydroxyl groups (Smith and others, 1991, this Proceedings). A net positive surface charge is expected at pHs below the point of zero charge (pH 7-9 for pure HIO) (Parks, 1967). Modification of surface charge can also occur as a result of adsorption of cations or anions; anion sorption is especially important at low pH. In most natural waters, suspended particles have a net negative charge. This observation has been related to the presence of organic coatings on suspended particles (Hunter and Liss, 1982) resulting from sorption of organic matter by the particles. Sorption of dissolved organic carbon (DOC) in acidic streams by HIO has been shown to be an important geochemical process and selectively removes fractions of organic matter (D.M. McKnight, U.S. Geological Survey, written commun., 1990). In acid mine drainage systems, extensive fresh HIO surfaces and low DOC concentrations allow the existence of positively charged surfaces (Newton and Liss, 1987; Ranville and others, 1989). Sulfate ion is weakly sorbed at low pH and can partly neutralize hydrous metal-oxide surfaces but has been shown not to produce a net negative surface charge (Rajan, 1978).

HIOs are formed in acidic streams by oxidation of ferrous iron sulfides, subsequent hydrolysis of ferric iron, and resulting precipitation of the HIO phase (Nordstrom and others, 1979). HIOs generally form as small particles with high specific surface areas. As a consequence of these high specific surface areas and the presence of strong metal-binding surface sites, these minerals are good sorbents for metals (Dzombak and Morel, 1990). Modification of HIO surfaces by sorbed or coprecipitated anions may enhance their sorptive capacities. Incorporation of silica into HIO has been shown to enhance cadmium sorption (Anderson and Benjamin, 1985). Sorption of DOC increases sorption of copper on HIO (Tipping and others, 1983) and aluminum oxides (Davis, 1984).

Because HIO formation occurs in the presence of organic matter, incorporation of organic matter into the structure of the newly formed HIO (coprecipitation) may be important. This would result in less surface-active HIO-associated organic matter than would be the case for sorbed DOC, possibly limiting the effect of organic matter on surface charge and adsorption characteristics of HIO.

The purpose of this paper is to present the results of field and laboratory studies investigating the role of organic matter in affecting the electrophoretic mobility (EM) of particles in acid-mine drainage systems. The goal of this study was to investigate how coprecipitation and(or) sorption of organic matter with HIO affects the EM of HIO particles. This was accomplished both by evaluating field data and performing laboratory experiments. The results will aid in understanding the surface chemistry of HIO in St. Kevin Gulch and in acid-mine drainage systems in general, which may affect the modeling of metal transport in these systems.

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EXPERIMENTAL

Field study

Samples of water and suspended sediment were collected from a number of sites along St. Kevin Gulch (see fig. 1) over a 3-year period beginning in 1988. Field measurements of pH, temperature, and specific conductance were performed. Water samples collected included raw water and 0.1 µm (micrometer) filtered water (using track-etched polycarbonate membranes). Anion analyses were performed by ion chromatography (IC) on unacidified, filtered samples. DOC analysis was performed on glass fiber filtered samples using a high temperature persulfate oxidation method. Surface charge on the particles was determined by measuring the EM of particles present in the raw samples at ambient concentration using a light-scattering technique (Rees, 1987).

Two size fractions of suspended sediments were collected from large-volume water samples (60 L (liters) or more) that had been screened through a 63-µm nylon mesh. A direct filtration using 147-millimeter-diameter, 5-µm porosity, track-etched polycarbonate filters was used to collect a silt-sized fraction. Filters were changed after 4 L were processed to minimize clogging of the filter. A colloidal size fraction was obtained by tangential-flow ultrafiltration of the 5-µm filtrate using 100,000 molecular weight membranes. Suspended sediments were removed from both filter types by placing the filters individually into Teflon[4] bags along with some sample water and by gently rubbing the particles off of the filters from outside the bags. The resulting suspension was split into two parts, and half was freeze-dried for analysis. The other half was stored at 4°C (degrees Celsius) for future experiments.

Laboratory Experiments

In order to investigate coprecipitation and adsorption of DOC by HIO separately, laboratory experiments were performed under controlled conditions that simulated the stream. In the first set of experiments, synthetic HIO was precipitated by diluting and raising the pH of a stock ferric nitrate solution (1,000 mg/L (milligrams per liter) iron) to pH 4.0 in acid-washed polyethylene bottles. The initial iron concentration was 20 mg/L and generally greater than 90 percent of the iron precipitated. The precipitation was performed in the presence of sodium sulfate at sulfate concentrations ranging from 0 to 100 mg/L. In the sorption experiment, Suwannee River Fulvic Acid (SR-FA) was added approximately 8 hours after the precipitation had begun. SR-FA was chosen because it is well characterized and is considered a "standard" for humic substances. Details

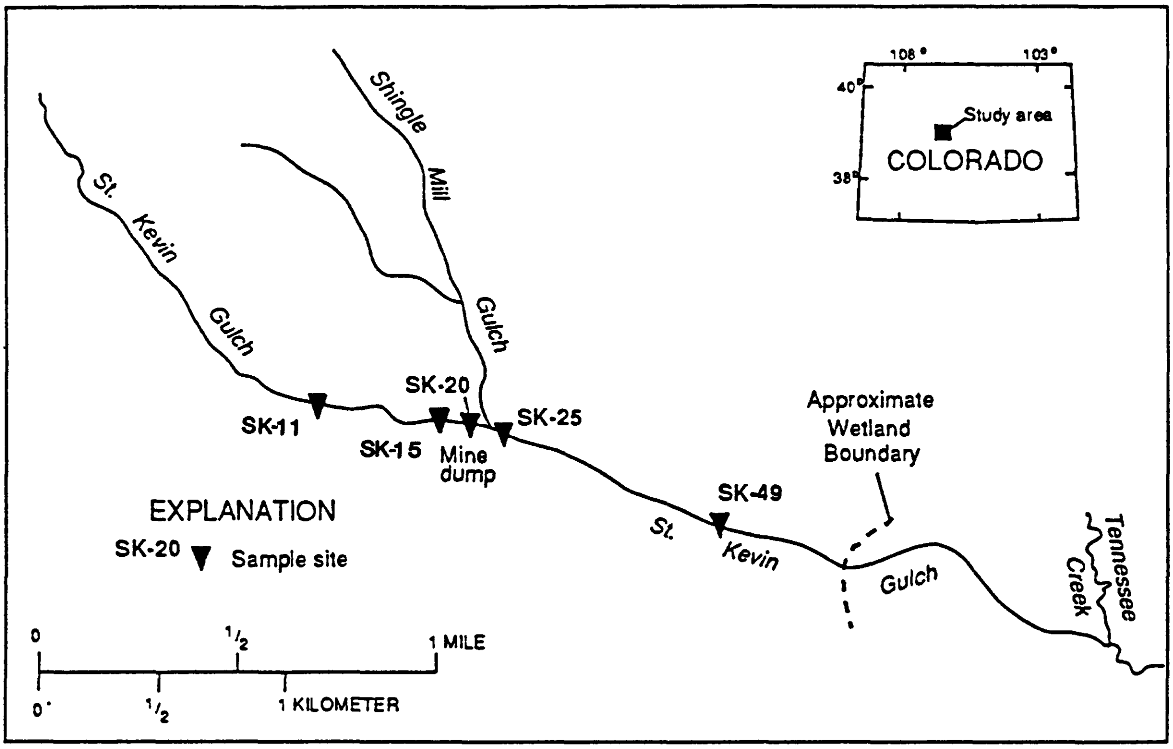

Figure 1. Sampling locations at St. Kevin Gulch, 1988-90.

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[4] The use of brand names in this paper is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

of its isolation and characterization are given in Averett and others (1989). In the coprecipitation plus sorption experiment, FA was added before the pH was raised so the precipitation occurred in the presence of the FA. The concentration of added DOC in the experiment was varied from 0 to 10 mg/L carbon. The experiment was allowed to equilibrate for a period of about 24 hours. The EM of the HIO were determined on aliquots of the suspensions. The solid phase was separated using centrifugation at 12,000 revolutions per minute for 1 hour in acid-washed polycarbonate centrifuge tubes, and the supernatant was decanted into acid-washed polyethylene bottles. Concentrations of metals in the supernatants were determined by ICP-AES, of anions by IC, and of DOC by persulfate oxidation.

In a similar experiment 100-mL (milliliter) samples of water collected from site SK-20 were diluted to a volume of 220 mL and the pH was raised to 4.0 to simulate the dilution and pH increase at SK-25 as a result of the addition of water from Shingle Mill Gulch, a near-neutral pH tributary (see fig. 1). No additional iron was added to the experiment so that the amount of HIO formed simulates the amount formed in the stream. The precipitation was performed in the presence of calcium sulfate at a final sulfate concentration of approximately 150 mg/L. Calcium sulfate was used instead of sodium so as to approximately match the major element chemistry of SK-25. Three types of organic matter were used to provide total organic carbon concentrations similar to those at SK-25 (0.7 - 2.6 mg/L carbon). These three types included SR-FA, a fulvic acid isolated from Shingle Mill Gulch (SMG-FA) by procedures outlined in Thurman and Malcolm (1981), and a rotary-evaporated concentrate of Shingle Mill Gulch water, here referred to as whole dissolved organic matter (SMG-DOM). The organic matter was added prior to the precipitation of HIO and, therefore, the experiment represents both coprecipitation and sorption. In the first set of experiments, centrifugation was more effective at phase separation for some samples than others. For consistency in this experiment, therefore, phase separation was accomplished by vacuum filtration with 0.1 μm polycarbonate filters. To remove carbon bleed from the filters, a washing scheme was devised that employed passing 75 mL of 0.1 molar NaOH, then 50 mL of pH 2 nitric acid, and finally 200 mL of distilled water through the filters. After washing, filtered distilled water had a DOC concentration similar to that of unfiltered distilled water. The filtrate was analyzed for DOC, metals, and anions. Aliquots of the unfiltered suspensions were acidified to dissolve the HIO; they also were analyzed for DOC, metals, and anions. EMs of the HIO suspensions were determined.

RESULTS AND DISCUSSION

The relation between DOC and EM of suspended sediments in St. Kevin is shown in figure 2. Increasing DOC concentration results first in a neutralization, then a reversal of EM from positive to negative. Generally, stream pH remains in the range of 3.5 to 4.5--a range where HIO surfaces are expected to have a net positive charge. High values of DOC occur during spring runoff and likely reflect flushing of DOC from surrounding soils of the watershed. Negative charge on the particles arises from the presence of negative functional groups (primarily -COO$^-$) present in the organic matter that are not involved in the sorption to HIO surface sites. Concentrations of DOC decline to low values after runoff as the streamflow decreases to base flow. During base flow, concentrations of dissolved iron are high and the greatest amount of HIO precipitation occurs in the stream. The positive suspended sediments are likely a result of the formation of large amounts of HIO surfaces, and an insufficiency of DOC to provide an organic coating sufficient to neutralize or reverse the charge.

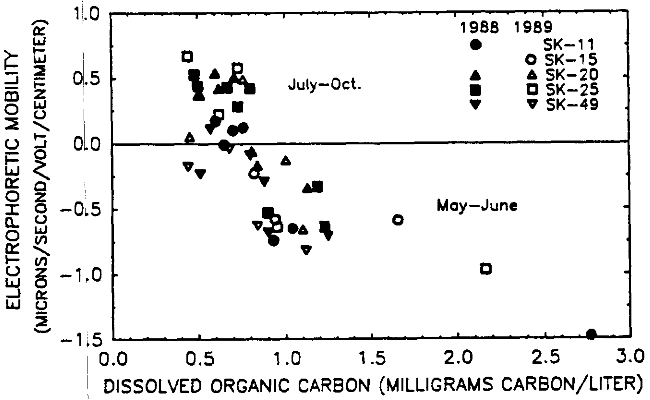

Figure 2. Relation of electrophoretic mobility of suspended sediment to that of dissolved organic carbon in St. Kevin Gulch, 1988 and 1989.

The direct relation between the organic carbon content and EM of the suspended sediments is shown in figure 3. Because EM of the total suspended sediments in the raw water samples was measured, weight percent carbon on the plot represents the average of weight percent carbon in the silt and colloid fractions. The values of weight percent carbon are surprisingly high (10-25 percent carbon) compared to typical suspended sediments, possibly reflecting several processes that incorporate organic carbon into the suspended sediments. Organic matter is strongly sorbed by HIO at low pH (Tipping, 1981; Davis, 1982) through a ligand-exchange mechanism (Stumm and others,

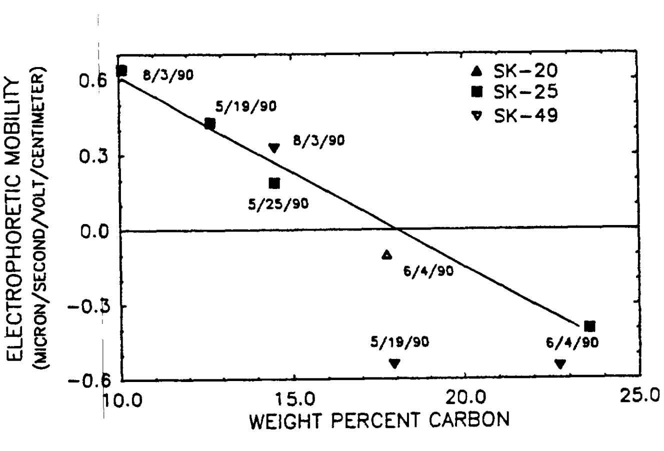

Figure 3. Electrophoretic mobility as a function of weight percent carbon for suspended sediments in St. Kevin Gulch, 1990. Linear regression drawn through SK-25 data only.

1980). Organic-matter sorption has been shown to be important in acidic streams (D.M. McKnight, U.S. Geological Survey, written commun., 1990). The mechanism whereby organic matter sorbs to positive HIO sites through a carboxyl group (Stumm and others, 1980) can be represented by

$$S - Fe - OH_2^+ + R - COO^- = S - Fe - OOC - R + H_2O,$$

where

S represents the bulk of the solid phase, and

R represents the rest of the organic matter, which contains additional negative sites that may not be involved in sorption to the HIO surface.

SR-FA, on average, contains four carboxyl groups per "molecule" (Leenheer, 1989). It is likely that not all these groups will be favorably situated near the surface and will, therefore, not interact with positive sites on the HIO. These groups can then provide a net negative charge to the surface, provided sufficient organic matter is present to neutralize the positive sites. In addition to coprecipitation and sorption of organic matter, biological processes also may account for the elevated concentrations of organic carbon in the suspended sediment. Suspended sediments can also provide a good substrate for growth of bacteria; abundant bacteria have been observed in suspended sediment samples from the site by epifluorescence microscopy (K.S. Smith, U.S. Geological Survey, written commun., 1990). Furthermore, bacteria have been shown to act as nucleating sites for the precipitation of HIO (Ferris and others, 1989). As shown in figure 3, organic carbon content in the suspended sediment increases from mid-May to early June; the highest concentrations prevail during spring runoff, which peaks in late May-early June. This period coincides with the period of elevated DOC concentrations and the most negative suspended sediment EM values. The lower DOC concentrations during August occur during the time of extensive HIO formation and coincide with the presence of positive suspended sediments. The very strong linear relation (r = 0.996) for site SK-25 is also somewhat surprising as the relative importance of the aforementioned processes, which incorporate organic matter into the sediments, might be expected to vary during the year and these processes would not be expected to affect the EM of HIO in identical ways. This result may indicate that a single mechanism is dominant.

The results of the first set of experiments designed to compare sorption only to coprecipitation plus sorption are shown in figures 4a and 4b, respectively. Not all data points are represented as several suspensions could not be separated by centrifugation. These samples corresponded to those with the highest positive or negative charge. The degree of aggregation of the HIO suspensions was observed to depend on the charge of the HIO particles; the most aggregation occurred in the suspensions of near neutral particles. This is in keeping with the electrostatic-stabilization theory of colloid stability (Hunter, 1981).

Particles have more negative EM by sorption of DOC than by coprecipitation plus sorption of DOC, probably because of incorporation of organic matter into the rather amorphous structure of the HIO during coprecipitation. Because EM is a measure of charge in the outer, diffuse layer of the particles, negative groups present on organic matter within the particle (if they exist) will not affect this measurement. It is also likely that organic matter within the HIO particles is completely neutralized. Final DOC concentrations are higher in the sorption-only experiment than in the coprecipitation-plus-sorption experiment, particularly for the highest DOC concentrations. This indicates that additional removal of DOC occurred in the coprecipitation-plus-sorption experiment because these data represent the 10 mg/L of carbon added in both experiments. In addition, sulfate strongly reduces the net positive charge on the HIO particles at low DOC concentrations but becomes less important at higher DOC concentrations. Comparison of figures 4a and 4b to figure 2 indicates that the experimental results mimic the field data quite well. From this comparison, however, it is not possible to make a conclusion on the relative importance of sorption compared to coprecipitation plus sorption as controlling processes in the stream.

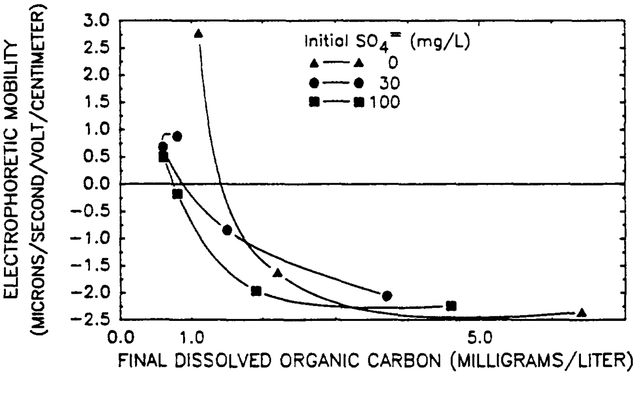

Figure 4a. Effect of sorption of Suwannee River fulvic acid on the electrophoretic mobility of HIO in the presence of $SO_4^=$ at pH 4.00 ± 0.05.

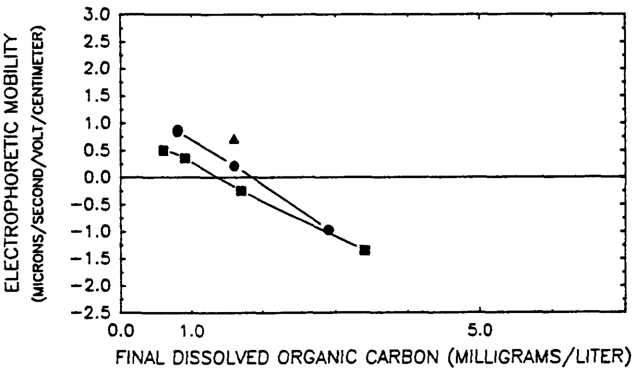

Figure 4b. Effect of coprecipitation of Suwannee River fulvic acid on the electrophoretic mobility of HIO in the presence of $SO_4^=$ at pH 4.00 ± 0.05.

The results of the second set of experiments comparing the relation between different organic matter sources and EM of precipitated HIO in simulated SK-25 water are shown in figure 5. The results indicate that SR-FA has a much greater effect on EM than either the SMG-FA or SMG-DOM. A possible explanation for this may come from the nature of the environment from which these organic matters were isolated. The SR-FA was isolated from a black water swamp and represents organic matter that has had little or no contact with mineral soils. The SMG-FA and SMG-DOM, however, were isolated from a low-DOC concentration stream situated in a rocky, subalpine watershed. Processes that cause adsorption and fractionation of organic matter onto HIO may already be occurring in the weathering soils of the watershed. In other words, the very process being studied in the laboratory experiments may have already occurred, to some extent, in the soils of the watershed. As a result, SMG-FA and SMG-DOM may be less reactive than SR-FA with respect to its electrical-charge characteristics. The smaller effect of SMG-FA, which comprised approximately 50 percent of the DOC in Shingle Mill Gulch, on EM as compared to SMG-DOM may be explained by the importance of charged organic components not isolated in the FA fraction. Complete interpretation of the differences in the amount of charge-modification by these various organic matter fractions await a more complete characterization of these fractions.

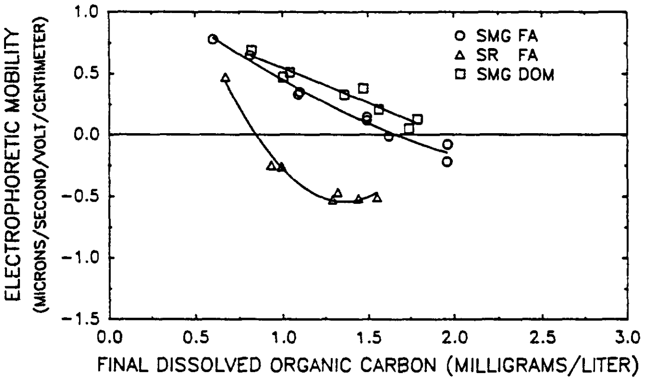

Figure 5. Coprecipitation of three organic matters with HIO formed from dilution and pH adjustment (pH 4.0) of SK-20 water collected on 9/18/90. Background $SO_4^=$ was approximately 150 mg/L.

ACKNOWLEDGMENTS

The authors wish to acknowledge the assistance of B. Kimball and the entire Upper Arkansas River group. Special thanks to J. Leenheer and G. Aiken for valuable discussions on the nature of humic substances. Suwannee River fulvic acid was provided by J. Leenheer.

SUMMARY

It is clear that a strong relation exists between the EM of suspended sediments in St. Kevin Gulch and both the organic carbon content of the suspended sediments and the DOC concentration. Seasonal variation in EM results from variation in organic matter present and in the amount of HIO being formed. Increases in DOC and percent carbon in the sediment accompany spring runoff and result in negatively charged suspended sediments. Sorptive and biological processes are likely explanations for the very high weight-percent-carbon values found for these suspended sediments. Suspended sediments are positively charged during the low-flow conditions of midsummer, probably a result of an insufficiency of DOC to neutralize the extensive HIO surfaces formed during this time.

Laboratory experiments indicate coprecipitation plus sorption removes more DOC than does sorption only, but this sediment-associated organic matter has less effect on particle EM. This observation likely reflects a paucity of organic matter on the actual particle surface because of the burial of organic matter within the HIO matrix. Comparison of several organic-matter types indicate SR-FA has the greatest effect on particle EM, possibly because of the source and history of the organic matter. SR-FA may be more reactive than SMG-FA or SMG-DOM due to its lack of contact with mineral soils that may remove the components most reactive with respect to charge modification of HIO surfaces. Further characterization of the three organic matters examined is required to interpret the results fully.

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PARTICULATE AND COLLOIDAL ORGANIC MATERIAL AND ASSOCIATED TRACE METALS IN PUEBLO RESERVOIR, COLORADO

By Diane M. McKnight[1], James F. Ranville[1], and Richard A. Harnish[1]

ABSTRACT

The chemical characteristics of particulate organic carbon in Pueblo Reservoir, Colorado, were examined. The Arkansas River is the major inflow to this reservoir. Four particulate organic carbon fractions were isolated by sedimentation, cross flow-ultrafiltration, and centrifugation. A silt fraction, two organic colloid fractions, and a mineral colloid fraction were obtained. The silt comprised 56.1 percent of the sediment mass and included intact planktonic diatoms, whereas the organic colloid fraction comprised 13.7 percent of sediment mass, 40 percent of the organic carbon, 60 percent of the organic nitrogen, and 61 percent of the lipid content. The carbon-^{13}*-nuclear-magnetic-resonance-spectrum for the organic colloid showed enrichment in carbohydrates and depletion in aromatic moieties. These results indicate that algal material may be the dominant source of the organic colloidal fractions. Iron, manganese, and zinc were enriched in the organic and mineral colloids, demonstrating the importance of these fractions in transport of trace elements.*

INTRODUCTION

Particulate and colloidal organic material in natural waters is composed of living and senescent organisms, cellular exudates, and partly-to-extensively degraded detrital material, all of which may be associated with mineral phases. Determination of the nature of this material has recently been an active research area because of the importance of particulates in the transport of trace-element and organic contaminants. For trace elements, sorption on particle surfaces is probably the dominant interaction. Most particles in natural waters are negatively charged (Hunter and Liss, 1979, Gerritsen and Bradley, 1987), and these negatively charged particles have the potential to sorb cationic metal ions. Specific metal-binding sites can also be involved in sorption. Carboxylic acid groups are the major acidic functional groups in dissolved and particulate aquatic humic substances; these groups can form charge-transfer complexes with several trace metals (such as copper (Cu), iron (Fe)) and strong complexes with other metals (such as aluminum). Another class of metal-binding sites are amino acids, which also form strong trace-metal complexes.

We conducted a study of particulate and colloidal organic material collected from Pueblo Reservoir, Pueblo, Colo., to examine the relations among sources of organic material, chemical characteristics of particulate and colloidal material, and interaction of organic material with trace elements. Although Pueblo Reservoir is an oligotrophic system, we expected that algal sources would account for most of the particulate organic carbon (POC), as we have observed in an alpine Rocky Mountain lake (McKnight and others, 1988). This paper presents the chemical characteristics of organic material from one site in Pueblo Reservoir, and discusses these results in the context of trace metal transport.

SITE DESCRIPTION

Pueblo Reservoir (fig. 1) is the water supply for the city of Pueblo, Colo., and is also used for recreation and fishing. The region is semiarid. The reservoir is fed by the Arkansas River, whose headwaters originate in the Rocky Mountains near Leadville, Colo. Several streams entering the Arkansas River have elevated trace-element concentrations from mine drainage (Kimball and others, 1989). The poor survival of trout in the Arkansas River has been attributed to elevated concentrations of lead (Pb), Cu, and zinc (Zn). The water sampled from the reservoir had a high sulfate concentration (table 1), possibly reflecting mine-drainage sources in the Arkansas River watershed, weathering of Cretaceous shales, and (or) the general aridity of the watershed. The phytoplankton was dominated by cryptophytes (*Chroomonas* sp. and *Cryptomonas erosa*) and diatoms (*Asterionella formosa* and *Fragilaria crotonensis*) (Ranville and others, 1991).

METHODS

Sample Collection and Fractionation

A large-volume surface-water sample (220 liters) was collected from Pueblo Reservoir on February 23, 1990. A combination of settling, tangential-flow ultrafiltration, and centrifugation were used to obtain four solid-phase fractions. A 41-hour settling period was used to separate the >2 to 5-µm (micrometer) fraction which we termed silt. The colloid fraction (<2 to 5 µm; >100,000 daltons) was isolated by tangential-flow ultrafiltration and centrifugation was used to fractionate the colloids into three fractions: organic colloid, settled organic colloid, and mineral colloid.[2]

Elemental composition (carbon (C), nitrogen (N)) and lipid content of the silt and colloid fractions was determined by Huffmann Laboratories[3], Wheatridge, Colo. (Huffman and Stuber, 1985; Ranville and others, 1991). Analysis of the organic colloid fraction and a sample of the filtrate was performed by inductively coupled plasma-atomic emission spectroscopy as described by Ranville and others (1991). Organic-carbon functionality was determined by use of solid state carbon-^{13} nuclear magnetic resonance spectroscopy with cross polarization/magic angle spinning (^{13}C-NMR-CPMAS) on a Nicolet NT-150 wide-bore NMR spectrometer at the Colorado State University Regional NMR Center. The data were collected for 8 hours for the mineral colloid and 12 hours for the organic colloid and silt fractions. The line broadening was 50 hertz (Hz) for the mineral colloid and 20 Hz for the organic colloid and the silt.

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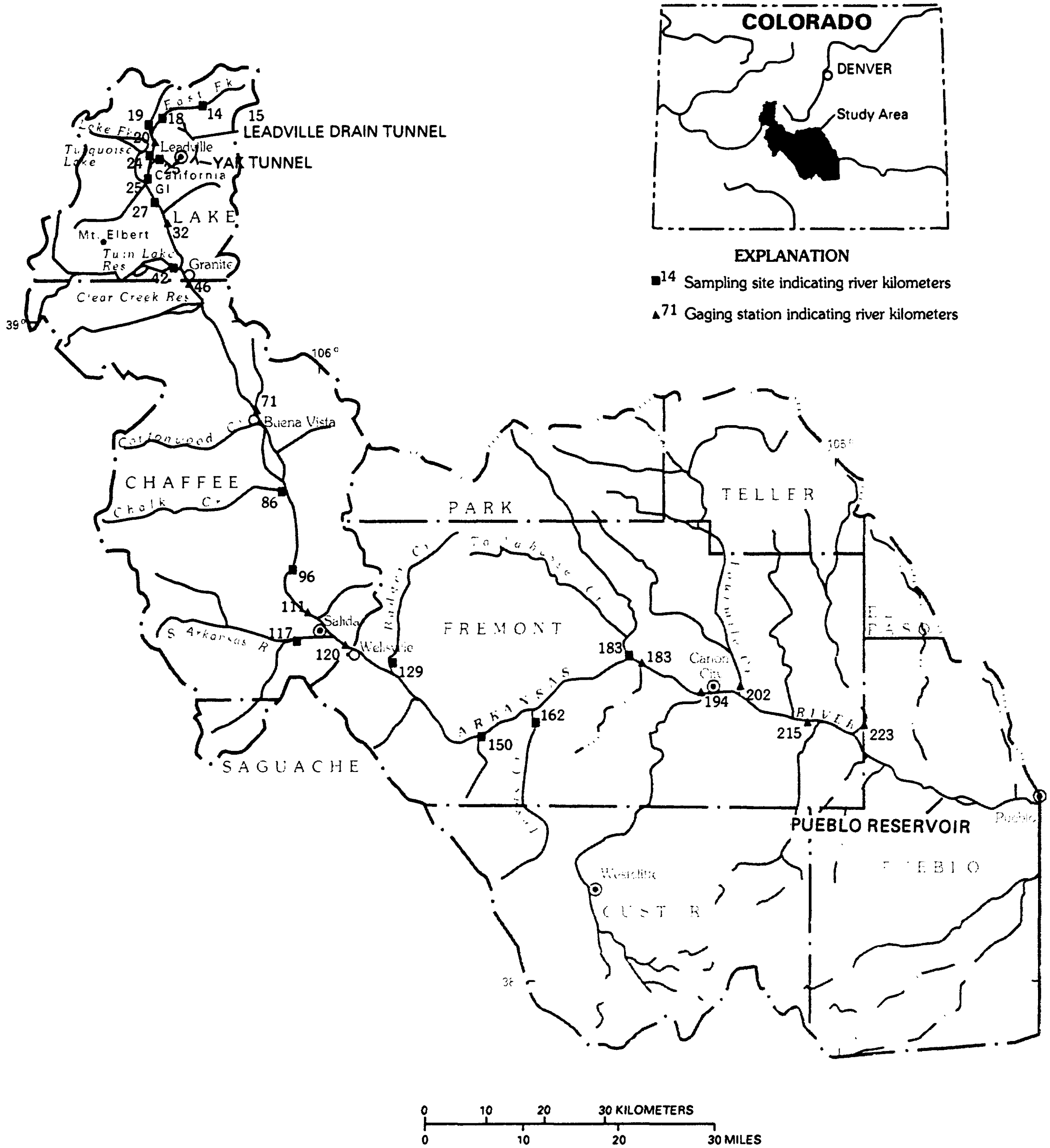
[1] U.S. Geological Survey, Denver, Colo.

[2] Complete details of the sampling and particle isolation methods is provided in Ranville and others (1991).

[3] The use of firm names or trade names is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.


COLORADO
DENVER
Study Area
EXPLANATION
■14 Sampling site indicating river kilometers
▲71 Gaging station indicating river kilometers
East Fk
Lake Fk
Turquoise Lake
LEADVILLE DRAIN TUNNEL
YAK TUNNEL
Leadville
California Gl
LAKE
Mt. Elbert
Twin Lake Res
Granite
Clear Creek Res
39°
106°
Buena Vista
Cottonwood Cr
CHAFFEE
Chalk Cr
PARK
TELLER
105°
FREMONT
S Arkansas R
Salida
Wellsville
ARKANSAS RIVER
Canon City
EL PASO
SAGUACHE
PUEBLO RESERVOIR
Pueblo
PUEBLO
Westcliffe
CUSTER
14
15
18
19
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25
27
32
42
46
71
86
96
111
117
120
129
150
162
183
183
194
202
215
223
0 10 20 30 KILOMETERS
0 10 20 30 MILES

Figure 1. Location of study area.

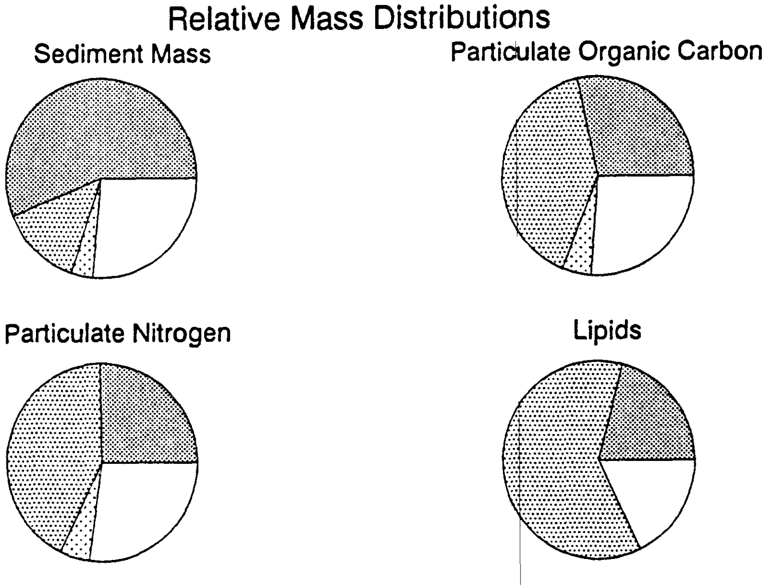
Table 1. *Chemistry of Pueblo Reservoir surface water sample collected on February 23, 1990, and of the organic colloid concentrate*
[NA,not analyzed; mg/L, milligrams per liter; μg/L, micrograms per liter; mg C/L, milligrams carbon per liter]

Chemical constituent	Concentration in filtered water[1]	Concentration in organic colloid	Ratio
Major ions			
Ca	62	92	1.5
Mg	19	24	1.2
Na	27	32	1.2
K	3	NA	-
Si	7	18	2.5
Sr	.68	.86	1.3
HCO_3	150		
SO_4	150		
DOC (mg C/L)	2.4		
Trace elements (μg/L)			
Al	<50	NA	-
Fe	<5	1,600	>550
Mn	<1	99	>99
Zn	8	160	21

RESULTS AND DISCUSSION

The settling method fractionated the sample into a component that has a high probability of settling through the water column to the bed sediments (silt), and a component that may be transported through the reservoir (colloids). The mass recovery of silt and colloidal material from the Pueblo Reservoir sample is shown in figure 2. The silt fraction contained most of the sediment mass (56.1 percent) and the settled organic colloid fraction contained the least (3.7 percent). The total recovery of suspended material was 870 mg (milligrams), corresponding to a concentration of 4 mg/L (milligrams per liter) in the whole water sample, with 488 mg in the silt and 387 mg in the colloid fractions. Measurements of the electrophoretic mobility of the four fractions yielded a result of -0.88 ± 0.08 μm/s^{-1} .V/cm^{-1} (micrometers per second per . volt per centimeter) for a whole water sample, and results ranged from -0.93 ± 0.04 μm/s^{-1}.V/cm^{-1} (organic colloid) to -0.88 ± 0.07 μm/s^{-1}.V/cm^{-1} (mineral colloid) for the different fractions (Ranville and others, 1991). These results confirm that these particles are negatively charged. The uniformity of the results may indicate that sorbed organic material controls the surface charge on all of the fractions (Tipping and Cooke, 1982).

Comparison of the inorganic chemistry of filtrate from the isolation of the colloids to the inorganic chemistry of the organic colloid concentrate is shown in table 1. Most of the major elements have comparable concentrations in both phases indicating they are primarily dissolved components. Fe, manganese (Mn),



	Percent Distribution	Sediment mass	Particulate organic carbon	Nitrogen	Lipids
▩	Silt	56.1	28.4	24.3	21.0
▦	Organic Colloid	13.7	40.6	40.7	61.1
▨	Settled Organic Colloid	3.7	4.9	6.0	0
☐	Mineral Colloid	26.5	26.1	29.0	17.9

Figure 2. Relative mass distribution (in weight percent) of sediment mass, organic carbon, nitrogen and lipids in the silt, organic colloid, settled organic colloid, and mineral colloid fraction from Pueblo Reservoir.

Table 2. *Chemical composition of the silt, organic colloid, settled organic colloid and mineral colloid fractions (in weight percent) from Pueblo Reservoir*

	Silt	Organic colloid	Settled organic colloid	Mineral colloid
Organic constituents				
Organic carbon	3.6	20	9.3	7.0
Nitrogen	.45	3.1	1.7	1.1
Atomic C/N	9.3	7.6	6.5	7.1
Lipids	.56	6.7	.01	1.0
Inorganic constituents				
Total				
Si	27	2.5	NA	35
Fe	1.5	0.8	NA	3.3
Mn (ppm)	450	1,800	NA	1,250
Zn (ppm)	200	350	NA	370
Metal/silicon ratio				
Fe/Si	5.4×10^{-2}	32.0×10^{-2}	—	9.3×10^{-2}
Mn/Si	0.16×10^{-2}	7.2×10^{-2}	—	0.35×10^{-2}
Zn/Si	0.07×10^{-2}	1.4×10^{-2}	—	0.10×10^{-2}

and Zn however, have significantly greater concentrations in the organic colloid fraction indicating they are in some way associated with this fraction. The ratio of Fe in the filtrate to Fe in the concentrate exceeds 500. Concentration ratios for Mn and Zn exceeded 99 and 21, respectively, also indicating association with the organic colloid fraction. Results from the total digestions (hydroflouric, nitric, hydrochloric, and perchloric are given in table 2. The ratio of Fe, Mn, and Zn to silicon (Si) is much higher in the organic colloid compared to the mineral colloid and silt, suggesting that trace elements in the organic colloid do not simply reflect the presence of detrital minerals in the organic colloid but imply additional association of trace elements with this phase. The association of these metals with the organic colloids is consistent with previous results showing the importance of organic complexation in trace-element transport (Buffle, 1988). Eisenreich and others (1980) showed in a study of the upper Mississippi River that the highest concentrations of Cu, cadmium (Cd), and Pb occurred in the 1 to 10,000K dalton fractions and correlated with organic-carbon content. In analysis of colloidal particles in the Patuxent River, Sigleo and Helz (1981) found that arsenic (As), antimony (Sb), selenium (Se), and Zn were enriched in the colloid fraction during the summer when the carbon content also increased.

The results of the analysis for organic C and N are presented in table 2. These results confirm that the organic colloid fraction is indeed enriched in organic C compared to the other fractions. Even though the organic colloid fraction comprises only 14 percent of the total sediment mass, it comprises 40 percent of the total particulate organic carbon (fig. 2). If we assume that the organic material in the organic colloid fraction has a carbon content of 50 percent (which is typical for aquatic humic substances), the organic carbon content of 20 percent corresponds to an organic colloid fraction consisting of 40 percent organic material. The settled organic colloid fraction had an organic carbon content intermediate between that of the organic colloid and mineral colloid fractions, and the silt fraction had the lowest organic carbon content. These data were used to calculate the total concentration of particulate and colloidal organic carbon of 0.28 mg C/L (milligrams carbon per liter), a value that is an order of magnitude less than the dissolved organic carbon (DOC) concentration of 2.4 mg C/L.

Nitrogen was distributed between the fractions in a similar manner as was the organic carbon (fig. 2). Comparison of C:N ratios (table 2) shows that the settled organic colloid fraction was the most nitrogen enriched and the silt fraction was the least. All the fractions contained organic material that was more enriched in nitrogen than are most aquatic fulvic acids, for which the C:N ratios range from 20 to 80. Lower values are found for freshwater fulvic acids derived from algal sources. Therefore, the C:N ratios for the Pueblo Reservoir material are consistent with algal and microbial biomass as the major source of organic material. These results may also indicate a greater protein content in the POC compared to that in the DOC.

The solid-state ^{13}C-CPMAS NMR spectra for the organic colloid, silt, and mineral colloid fractions are shown in figure 3. The spectrum for the organic colloid fraction shows excellent resolution of the major carbon moieties. The other two spectra are more poorly resolved and are probably affected by the lower carbon content and paramagnetic metals (Fe and Mn) in the inorganic part of the fractions. Six broad peaks are typically present in spectra of natural organic material: The first aliphatic peak (AL-I), 0 to 62 ppm (parts per million), represents carbons bonded to other carbons (methyl, methylene, and methine) as well as some carbons bonded to N or S. The second aliphatic peak

(AL-II), 62 to 90 ppm, represents carbons bonded to oxygen (carbohydrates, alcohols and ethers). The third aliphatic peak (AL-III), 90 to 110 ppm, represents anomeric carbons. The aromatic peak (AR), 110 to 165 ppm, represents primarily sp^2-hybridized carbons (aromatic carbons and other double bonded carbons). The first carbonyl peak (C-I), 165 to 185 ppm, represents primarily carboxylic carbons and the second carbonyl peak (C-II), 185 to 220 ppm, primarily represents ketones.

In the spectrum for the organic colloid fraction, the C-II peak is not present, and the AR peak is present only to a very limited extent, accounting for only 8 percent of the total area of the spectrum. The minor presence of aromatic moieties suggests that this material is not derived from degradation of plant materials in the watershed. The AL-I peak represents 38 percent of the total area, and lipids are represented in this region. The ratio of the AL-III peak and the AL-II peak indicates that carbohydrates may comprise a large percentage of the organic carbon. Means and Wijayaratne (1984) found that colloidal organic material in an estuarine system was dominated by carbohydrates (35-60 weight percent). The presence of carboxylic acid groups indicated by the C-I peak suggest that some of the carbohydrates are present as sugar acids.

Despite the poor resolution of the spectra for the silt and mineral colloid fractions, a discrete peak in the upper part of the AL-I region of the silt fraction is evident, possibly corresponding to lipids. The overall carbon distributions for the silt and mineral colloid fractions are very similar, and these fractions are more enriched in noncarbohydrate aliphatic material than the organic colloid fraction. Although these results need to be interpreted cautiously, they may indicate that the greater hetero-atom content and polarity of the organic colloid fraction limits its sorption on mineral surfaces, as proposed by Means and Wijayaratne (1984).

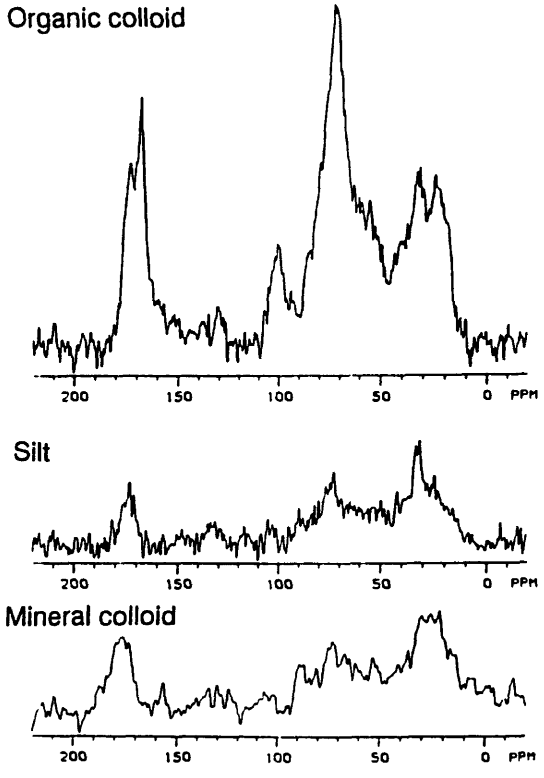


Figure 3. Solid state natural abundance Carbon-13 nuclear magnetic resonance spectra of particulate and colloidal fractions from Pueblo Reservoir, Pueblo, Colorado. These spectra consist of major broad peaks characteristic of aquatic humic substances.

As shown in table 2 and figure 2, the organic colloid fraction had the highest lipids content followed, in decreasing order, by the mineral colloid, the silt, and finally the settled organic colloid. The bulk of the total lipids (61.1 percent) was contained in the organic colloid fraction, which was 6.66 percent lipids by weight (fig. 2). In contrast, Means and Wijayaratne (1984) found that lipids comprised less than 1 percent of the estuarine organic colloids. However, based on the comparison of peak area of the Al-I region, compared to that of the other regions of the ^{13}C-CPMAS-NMR spectra, the silt and mineral colloids were more lipid-rich. This discrepancy may be explained by (1) sorption of lipids to mineral surfaces and interlayers in the clay-rich fractions (silt and mineral colloids) which prevents extraction, and(or) (2) inclusion of aliphatic carbons in the Al-I region in molecules other than lipids that are not soluble in chloroform-methanol. The significant presence of lipids in the organic and mineral colloids reflects the algal source of POC in Pueblo Reservoir. Among algae, diatoms (the greatest biomass of algae in Pueblo Reservoir) are lipid-rich and can consist of up to 70 percent lipids by weight (Tissot and Welte, 1984).

CONCLUSIONS

In Pueblo Reservoir, a primarily algal source yields particulate and colloidal organic matter low in aromaticity and rich in carbohydrates, organic nitrogen, and aliphatic lipids. Fe, Mn, and Zn were concentrated in the organic colloid fraction, indicating that organic colloids may be important in the downstream transport of trace-element contaminants.

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CALCULATION OF CONSERVATIVE-TRACER AND FLUME-DISCHARGE MEASUREMENTS ON A SMALL MOUNTAIN STREAM

By Gary W. Zellweger[1] *and* Wendy S. Maura[2]

ABSTRACT

An experiment was conducted to (1) determine which sections of a reach of a stream were losing water, (2) test if a sequence of three simultaneous lithium-tracer injections spaced along the 231-meter reach could detect the loss, and (3) compare discharge measurements from three 3-inch Parshall flumes with discharge calculations from the tracer-dilution method. Results indicate that about 2 liters per second, approximately 20 percent of the discharge, was being lost in the lower half of the study reach. The multiple tracer-injection method was able to detect the loss and to determine where in the reach the loss was occurring. Flume-discharge measurements also indicate the loss but did not agree with the tracer-dilution discharge measurements at all sites.

INTRODUCTION

Each year during August, when discharge is about 10 L/s (liters per second), the lower reach of St. Kevin Gulch, Lake County, Colo., loses water by a combination of evaporation, percolation, or transpiration, resulting in the complete disappearance of the stream a few hundred meters below an area of ongoing research (McKnight and others, 1988). A field experiment was conducted at this stream on August 29, 1989, with three purposes: (1) to determine from discharge calculations which parts of the stream reach were losing water; (2) to test whether three tracer injections spaced along the stream could be used to calculate discharge simultaneously at three locations in a stream that loses water, and (3) to compare discharge measurements calculated from tracer dilution with those obtained using portable modified Parshall flumes. This paper presents the results of the experiment.

DISCHARGE MEASUREMENTS

Tracer-Dilution Method

Ionic tracer injections have been used previously to measure discharge, traveltime, dispersion, storage volumes, and one-dimensional model parameters (Bencala, 1984; Jackman and others, 1984). In small, shallow streams with rough bottoms, when discharge is low, the tracer-dilution method is a practical alternative to calculating discharge from current-meter measurements (Zellweger and others, 1989). However, because the concentration of the tracer needs to be at least 0.5 milligrams per liter, the method is limited by practical restraints to streams with discharges of about 1,000 L/s or less.

In the tracer-dilution method, discharge is calculated by dividing the mass-addition rate of the tracer (the injection-pump rate times the tracer concentration of the injectant) by the increase in tracer concentration between the upstream sample location and a downstream sample location (Kilpatrick and Cobb, 1985). The method requires that the tracer be conservative--that is, not be lost because of reaction with the water or streambed. Complete mixing of the tracer is necessary, but the method is not otherwise affected by the morphology of the stream. A single tracer injection can be used to measure discharge at many downstream locations in a stream that is gaining water because water inflows dilute the tracer. In streams that are losing water, discharge can be calculated only at the point of tracer injection because water subsequently lost from the stream does not affect the concentration of tracer in the remaining water. Separate injections were thus necessary to obtain discharge at points along St. Kevin Gulch.

Parshall Flume Method

Parshall flumes are the primary means of measuring discharge in streams too small to use velocity meters. The 3-in. (inch) modified Parshall flume is 12 in. high, 18 in. long, 8 in. wide at the upstream end constricting to 3 in. at the downstream end. Discharge values for the 3-in. modified Parshall flume were read from a rating table and compiled by the Colorado district office of the U.S.Geological Survey using field measurements of water depth in the flumes. Under controlled conditions, the 3-in. Parshall flume has an uncertainty of less than 1 percent (Davis, 1963), but the uncertainty of flumes similar to those used in this work could vary by 7 percent according to Kilpatrick and Schneider (1983), who attribute the variation to imprecision in flume shape and suggest that flumes be calibrated separately. Two advantages of the Parshall flume method over the tracer-dilution method are cost, especially in labor, and the ability to measure discharge without the need to collect samples and wait for their analysis. Disadvantages are that flumes require some vertical gradient, and do not work well in coarse bottom streams or channels where the flow cannot be readily confined to the flume.

EXPERIMENT

Discharge was measured at three sites, 1878, 1981, and 2109. Each site name is the distance, in meters, downstream from a reference point established in previous work at St. Kevin Gulch (fig. 1). The reach between sites 1878 and 2109 had been suspected of losing water. Each site consisted of an upstream sample site, a tracer-injection point, a 3-in. modified Parshall flume below the injection point, and a downstream sampling site sufficiently distant from the

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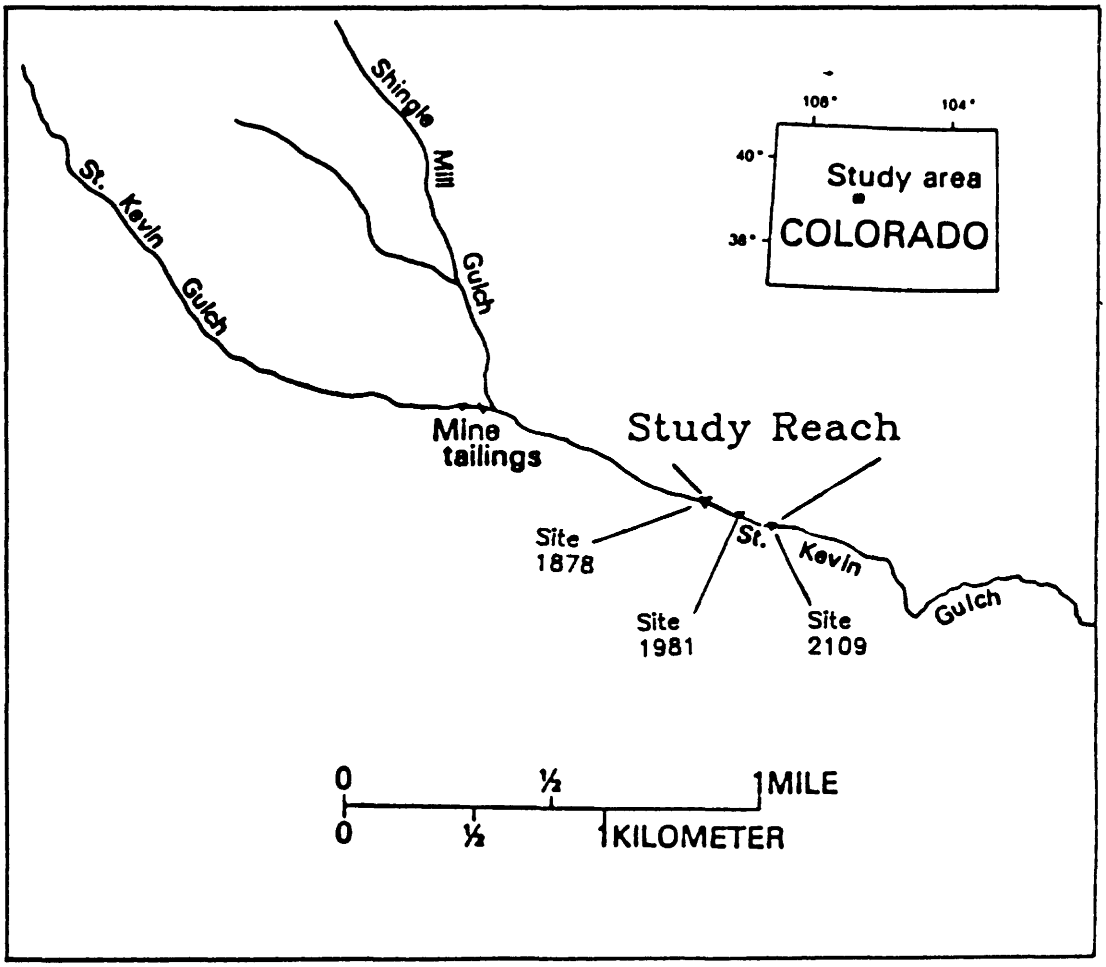

Figure 1. Site map showing location of the study reach relative to St. Kevein Gulch (From McKnight and others, 1988.) The site names are their distance downstream of a reference point (not shown).

injection point to allow for complete mixing of the tracer. A well-mixed lithium chloride solution was divided into three containers and injected at each site by an adjustable-rate, battery-powered, constant-flow pump. In streams with near-neutral pH, where lithium would be adsorbed onto the streambed, a suitable tracer would have been an anion such as chloride, bromide, or sulfate. However, the acidic nature of St. Kevin Gulch (pH~3.7) made it possible to use lithium (Bencala and others, 1990). Computational accuracy improves as the ratio of the downstream tracer concentration to upstream concentration increases (Zellweger and others, 1989). Thus, the rate at which tracer was added at the three sites was increased substantially at succeeding downstream sites. The injection at site 2109 began at 9:18 a.m. followed by an injection at site 1981 at 9:49 a.m., and at site 1878 at 11:00 a.m. Samples were collected in pairs above and below each injection. Measurements of the depth of water in the Parshall flumes were made approximately hourly. The concentration of lithium in the stream samples and in dilutions of the injection solutions were measured by atomic- adsorption spectroscopy. Discharge was calculated as described above; each measurement was calculated from a discrete sample below the injection point and from an interpolated value from above the injection point.

RESULTS

Discharge for the three sites as calculated from the dilution of the lithium tracer is shown in figure 2. Virtually, no loss of flow occurred between sites 1878 and 1981, and about 2 L/s was lost between sites 1981 and 2109. Discharge measurements by Parshall flume for the same sites are shown in figure 3. On the basis of the flume data a loss of about 1 L/s occurred between sites 1878 and 1981 and a loss of about 2 L/s occurred between sites 1981 and 2109. Both methods detected a decrease in discharge from morning to late afternoon. Analysis of lithium concentrations in streamwater that had traveled from site 1878 to site 1981 and from site 1981 to site 2109 indicated that no change in lithium concentration occurred over the distance between the sites. This indicates that the lithium tracer was conservative and that no water was gained by the stream.

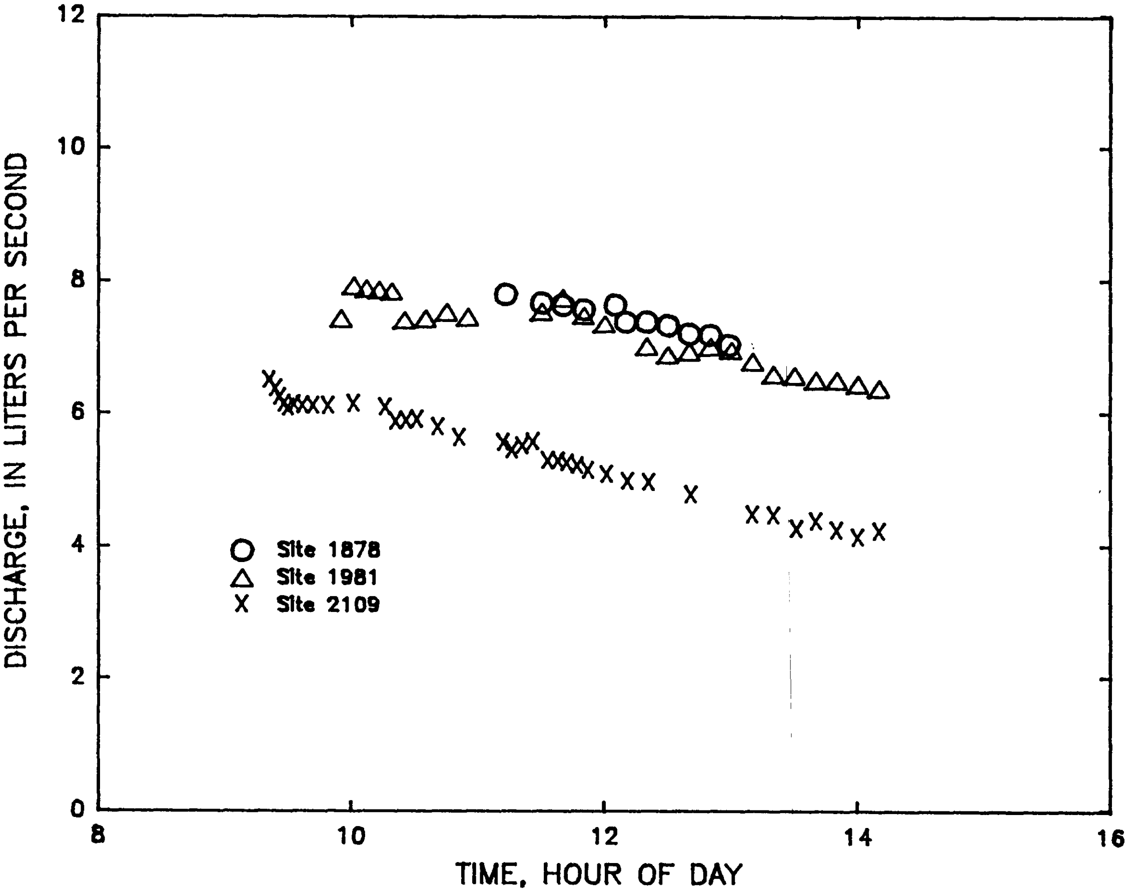

Figure 2. Discharge calculated on the basis of dilution of lithium tracer.

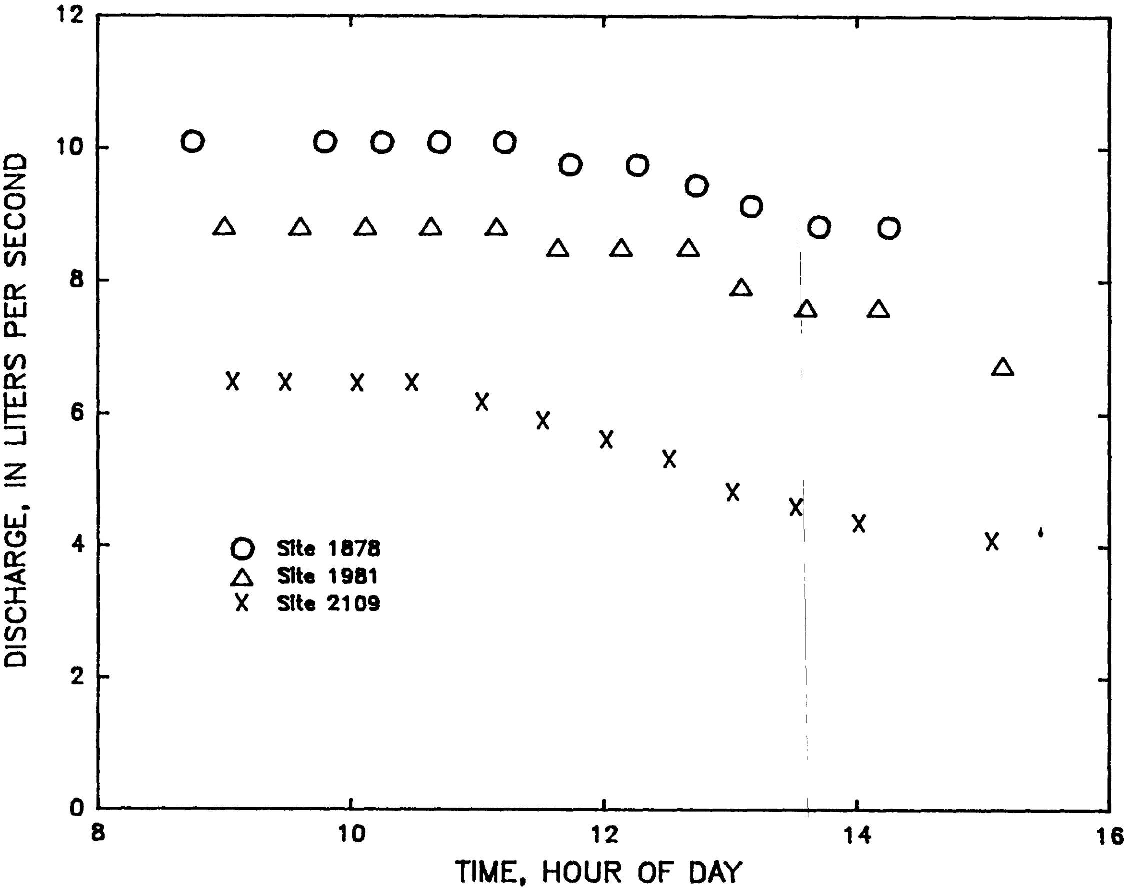

Figure 3. Discharge calculated on the basis of water depth in a 3-inch Parshall flume.

DISCUSSION

Both methods detected water loss over the length of the reach. Agreement between the two methods at site 2109 is good. Evaluation of the results at the two other sites shows that, although both methods detected a pattern of decreasing discharge during the day, there was a nearly constant difference of about 1 L/s between the methods at site 1981 and 2 L/s at site 1878. It is unknown whether this difference exceeds the variation that would be expected for the methods or if there was an error in one of the methods. Discharge measurement by the Parshall flume method is calculated from a single measurement that can easily be made with an accuracy of ±2 millimeters, equivalent to about 0.2 L/s. Accuracy, however, depends on proper positioning of the flume in the channel so that the rating curve is valid. The discharge measurements made by the tracer-dilution method were more variable than those made by the flumes, probably because the result of the 1 to 2 percent random error in the measurement of lithium concentration that was incorporated in the calculation of discharge. Errors in the installation of a Parshall flume generally produce readings less than the true discharge, but, at site 1878, discharge measured by the Parshall flume was greater than that measured by the tracer-dilution method. This suggests a possible error in the tracer-dilution discharge values calculated for site 1878.

SUMMARY

Discharge in small streams can be measured by using either small Parshall flumes or tracer-dilution methods. In this study, both methods were able to confirm that water was being lost in the reach between the sites 1981 and 2109, and to show that the late-afternoon discharge was less than the morning discharge. Differences in the results of the two methods at site 1878 indicate the need to determine which method is capable of substantial error.

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THE GLOBE, ARIZONA, RESEARCH SITE--CONTAMINANTS RELATED TO COPPER MINING IN A HYDROLOGICALLY INTEGRATED ENVIRONMENT

By James H. Eychaner[1]

ABSTRACT

Water moving from an area of copper mining has contaminated an arid-zone aquifer and perennial stream near Globe, Arizona, where traveltimes from precipitation to outflow are less than 15 years for ground-water paths entirely within unconsolidated alluvium. During dry climatic cycles, stream channels are ephemeral upstream from the perennial reach, but in wet cycles the aquifer fills and streamflow is continuous throughout the basin.

The most contaminated water contains more than 1,000 milligrams per liter of iron and sulfate and 100 milligrams per liter of aluminum and copper. A front at which pH falls below 5 has advanced through the alluvium at a rate of 0.2 to 0.3 kilometers per year during the past several decades and could arrive at the perennial reach within 6 to 8 years. Dissolved manganese concentrations in streamflow increased from 0.5 milligrams per liter in 1979 to about 35 milligrams per liter in 1988-89. At one streamflow station, dissolved nickel began to increase in 1988 and alkalinity began to decrease in 1989, but no change has been measured at another station 5 kilometers downstream. Aquifer cleanup began in 1987, but several years will pass before its success can be assured.

In the ground water, pH is controlled by reactions with carbonate minerals, by slower reactions with silicate minerals, and by production of hydrogen ions in metal-oxidation reactions. Dispersed gypsum crystals, iron-oxide coatings, and silicate minerals altered to clays are found in well cuttings from contaminated alluvium. In a mass-transport model of the advancing plume, calcite, dolomite, microcline, and manganese oxide dissolved from the aquifer, and ferric hydroxide, gypsum, and gibbsite precipitated. Manganese oxide in uncontaminated alluvium is an effective oxidant of ferric iron, but in column experiments about 7 moles of iron precipitated for each mole of manganese that dissolved; identification of the dominant terminal electron acceptors is uncertain.

As the ground water becomes perennial streamflow, gas exchange with the atmosphere causes carbon dioxide to decrease and oxygen to increase; manganese oxide minerals form on the streambed. About 0.9 mole of calcium dissolved from calcite for each mole of manganese that precipitated in a reaction-path model.

INTRODUCTION

Contamination related to a century of mining, principally for copper, in the Pinal Creek basin near Globe, Ariz. (fig. 1), has produced complex geochemical interactions among pH, mineral solubility, oxidation-reduction chemistry, and sorption in ground- and surface-water environments. Contaminated ground water has long been recognized in the area but was first quantified in 1983 (Envirologic Systems, Inc., 1983). Studies by the U.S. Geological Survey of contaminant transport and transformation processes began in 1984 (Eychaner, 1989). The principal contaminant was an acid ferrous sulfate solution of variable composition that included other metals and some organic compounds. Cleanup of the contaminated ground water began in 1987 under the supervision of the U.S. Environmental Protection Agency (1987; Arthur and Tolle, 1991, this Proceedings). This paper provides an overview of the geohydrologic system, the status of contamination in late 1990, and research in progress.

Underground copper mining began near Globe in 1882 and ended in 1931 (Peterson, 1962). Since 1903, copper has been mined near Miami, principally in open pits (fig. 1). Near Miami, ore minerals are disseminated in a granite porphyry. Chalcocite, chalcopyrite, and pyrite predominate in the deeper parts of the ore body, and chrysocolla, malachite, and azurite are common in the upper parts.

The mines and research sites lie in the surface drainage basin of Pinal Creek, which has an area of 505 km^2 (square kilometers) and slopes from 2,400 m (meters) above sea level in mountains at the southern boundary of the basin to 835 m at Inspiration Dam in the north. An aquifer occupies about 170 km^2 within the basin (fig. 1) including about 17 km^2 of unconsolidated alluvium. The alluvium, which conveys a large majority of the flow through the aquifer, occurs along Miami Wash, Pinal Creek, and tributary streams in a band 300 to 800 m wide. The alluvium is as much as 50 m thick and forms the upper, central part of the aquifer (fig. 2). Materials range in size from clay to boulders; fine sand to coarse gravel predominate. Finer and coarser materials generally are present in local lenses or stringers (Walter and Norris, 1991, this Proceedings).

Consolidated basin fill forms the remainder of the aquifer. The basin fill is 100 to 1,200 m thick and lies beneath and adjacent to the unconsolidated alluvium. Basin fill consists of unsorted angular rubble, well-rounded pebbles and cobbles, and well-cemented sand and silt (Peterson, 1962, p. 41-44).

Average precipitation of about 780 mm/yr (millimeters per year) in the mountains (Sellers and others, 1985) produces seasonal flow in small streams. Precipitation occurs as brief summer thunderstorms or as winter storms that may last several days. Snow accumulates in the mountains above an altitude of 2,000 m. Most recharge to the aquifer occurs along stream channels during winter and spring.

At the northern end of the basin, where average precipitation is 340 mm/yr, the aquifer is truncated by low-permeability rocks, and perennial flow results in Pinal Creek (figs. 1 and 3). Calculated traveltimes from precipitation to outflow are less than 15 years for ground-water paths entirely within the alluvium but hundreds of years for paths

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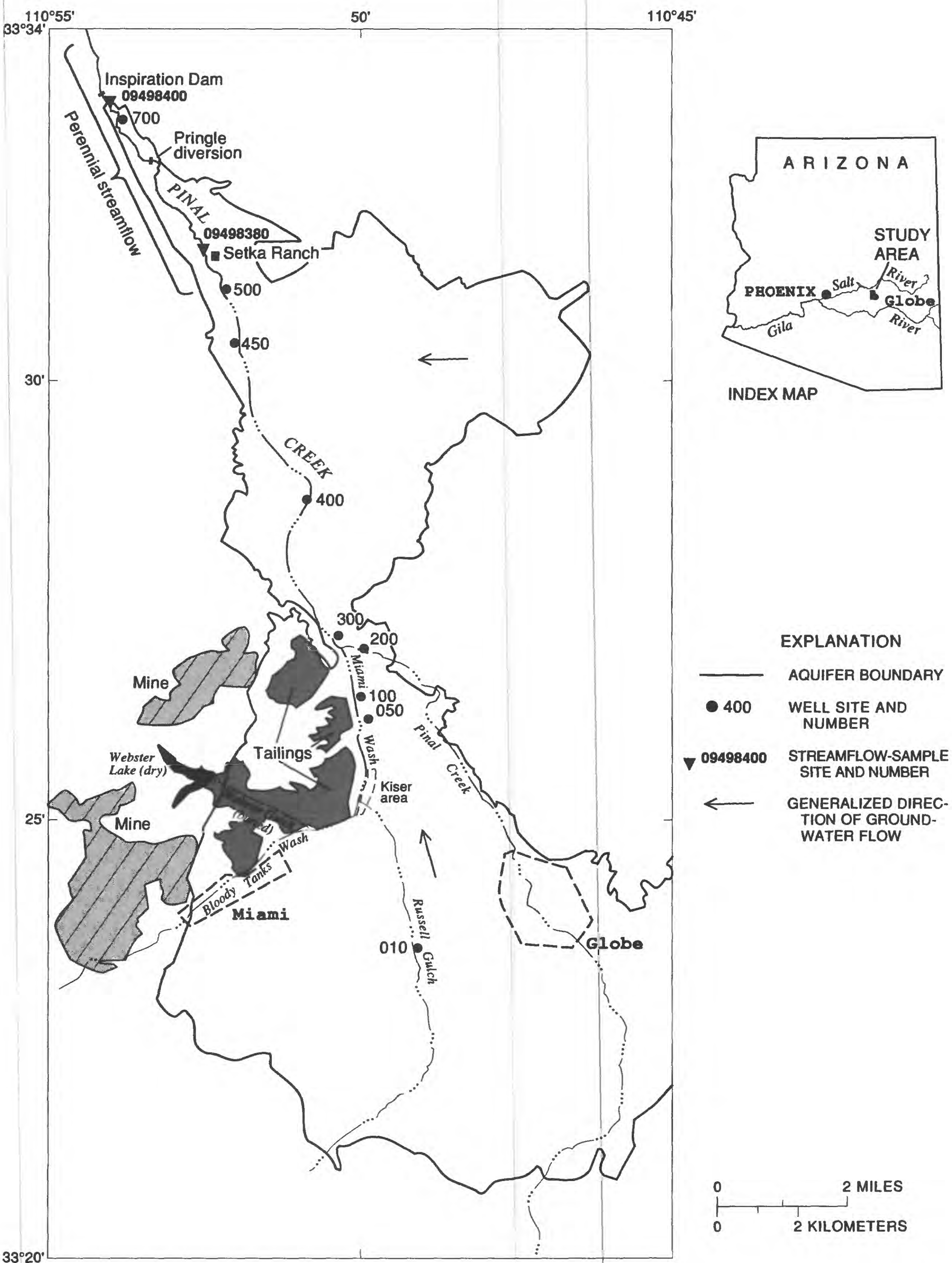
110°55'
50'
110°45'
33°34'
30'
25'
33°20'
Inspiration Dam
09498400
700
Pringle diversion
Perennial streamflow
PINAL
09498380
Setka Ranch
500
450
CREEK
400
300
200
Miami
100
050
Wash
Pinal
Creek
Mine
Tailings
Webster Lake (dry)
Kiser area
Bloody Tanks Wash
Miami
Russell Gulch
010
Globe
ARIZONA
STUDY AREA
PHOENIX
Salt
River
Globe
Gila
River
INDEX MAP
EXPLANATION
AQUIFER BOUNDARY
● 400 WELL SITE AND NUMBER
▼ 09498400 STREAMFLOW-SAMPLE SITE AND NUMBER
← GENERALIZED DIRECTION OF GROUND-WATER FLOW
0
2 MILES
0
2 KILOMETERS

Figure 1. Area of study.

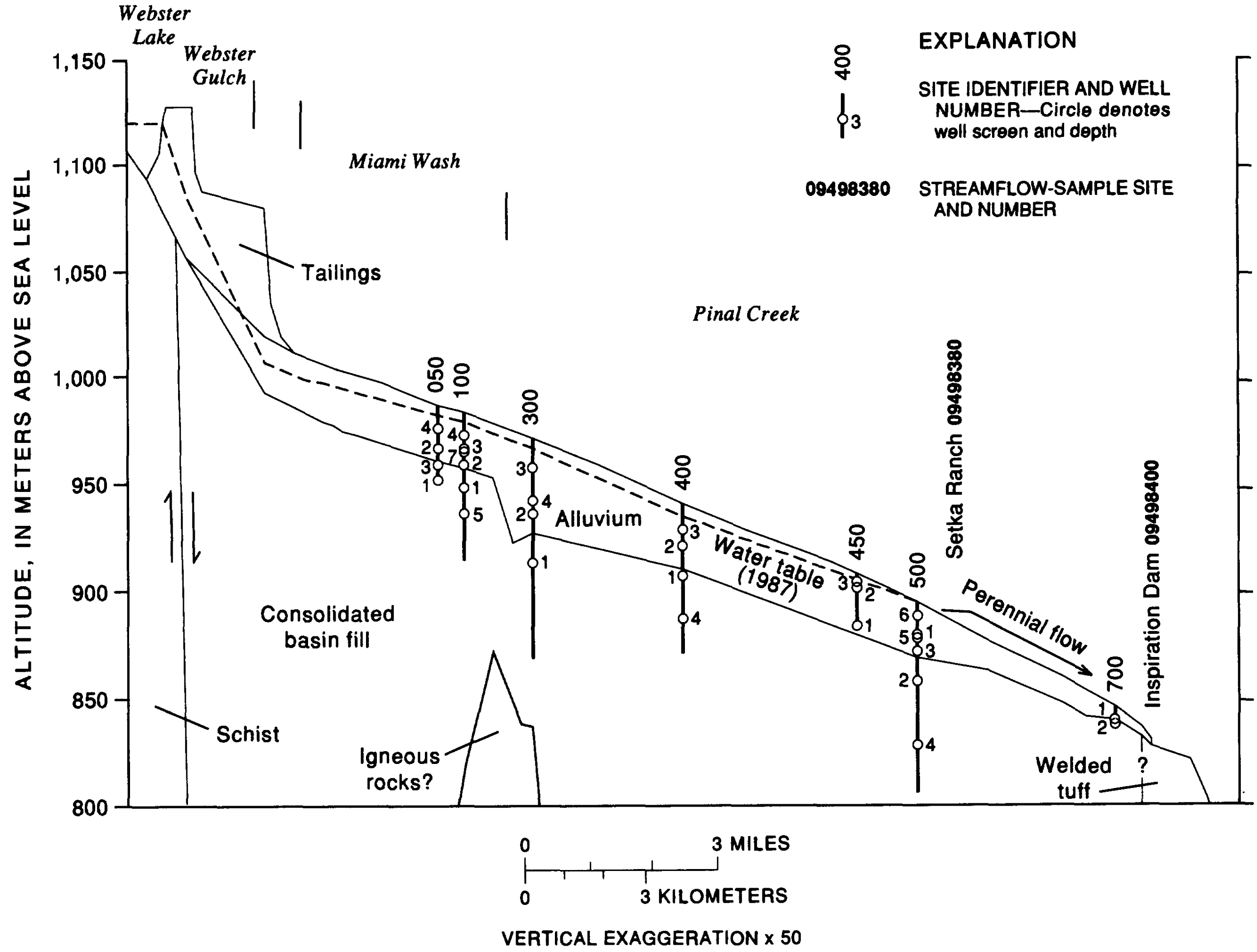
Webster Lake
Webster Gulch
Miami Wash
Tailings
Pinal Creek
Alluvium
Water table (1987)
Perennial flow
Consolidated basin fill
Schist
Igneous rocks?
Welded tuff
?
050
100
300
400
450
500
700
Setka Ranch 09498380
Inspiration Dam 09498400
ALTITUDE, IN METERS ABOVE SEA LEVEL
1,150
1,100
1,050
1,000
950
900
850
800
EXPLANATION
SITE IDENTIFIER AND WELL NUMBER—Circle denotes well screen and depth
09498380 STREAMFLOW-SAMPLE SITE AND NUMBER
0 3 MILES
0 3 KILOMETERS
VERTICAL EXAGGERATION x 50

Figure 2. Generalized hydrogeologic section of the aquifer. 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.

in the basin fill (Brown, 1991, this Proceedings). Average ground-water flow through the aquifer was estimated to be 0.27 m^3/s (cubic meters per second) (Hydro Geo Chem, Inc., 1989).

Ground-water levels and quality have been monitored since 1984 in wells near the stream channels (fig. 1). By June 1990, 32 wells in 9 groups had been drilled. The wells have short screened intervals at depths of 5 to 69 m (fig. 2). Water levels in upgradient wells rise or fall several meters per year, depending on recent recharge and withdrawals (fig. 3, well 401), but generally do not rise above the altitude of the streams (fig. 3, well 101). Water-level variations in downgradient wells are limited by the interaction of hydraulic conductivity, hydraulic gradient, and ground-water discharge to Pinal Creek. During dry cycles, stream channels are ephemeral from near the mountains to the perennial reach, but in wet cycles the aquifer fills and streamflow is continuous throughout the basin. Following a wet extreme, interrupted flow occurs for several months to a few years in areas of lower aquifer transmissivity, such as near the confluence of Miami Wash and Pinal Creek.

In 1990, perennial flow began about 6 km (kilometers) upstream from streamflow-gaging station 09498400, Pinal Creek at Inspiration Dam (fig. 1), where discharge and water quality have been monitored since 1979. The dam is an abandoned diversion structure that is filled to the crest with sediment. The beginning of perennial flow moved downstream about 600 m during 1988 and 1989. In March 1990, about 40 percent of the discharge from the aquifer occurred in the first 600 m of streamflow (Faires and Eychaner, 1991, this Proceedings, fig. 2). Gaged discharge from the aquifer to the stream was 0.1 to 0.4 m^3/s during 1980-89 (fig. 3), and about 0.09 m^3/s was diverted for industrial use 2 km upstream from the dam. Since 1987, additional water-quality samples have been collected 5 km upstream from the dam at station 09498380, Pinal Creek at Setka Ranch (fig. 1). Analytical data were reported by Eychaner and others (1989) and Brown (1990).

OCCURRENCE AND MOVEMENT OF CONTAMINANTS

Acidic waste solutions of unknown composition were common in the mining area west of Miami Wash before

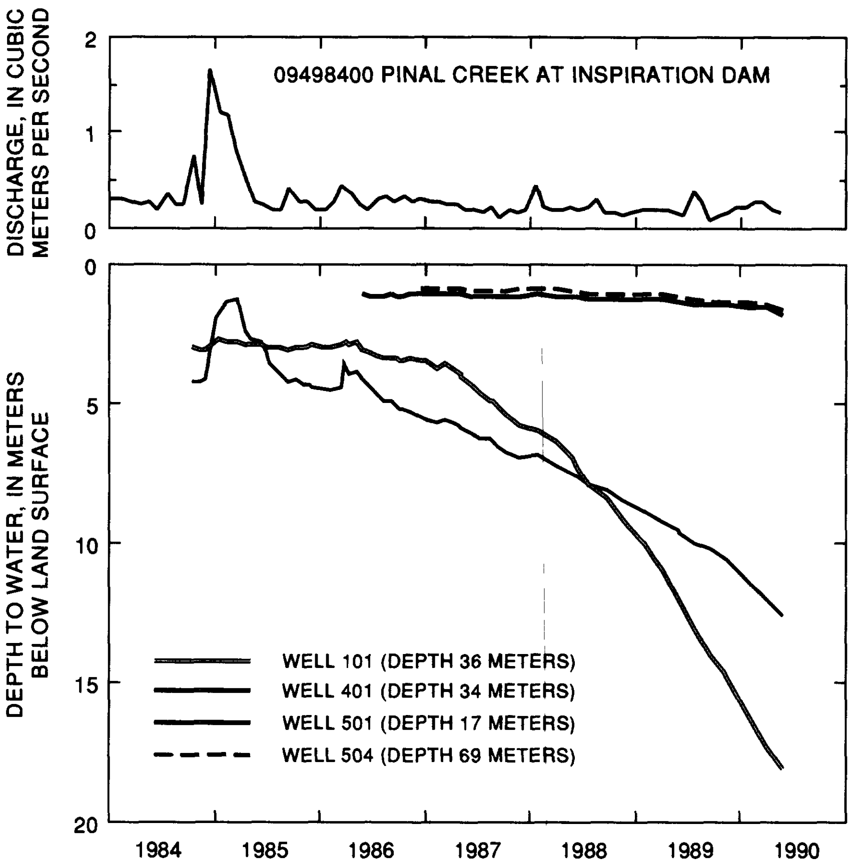

Figure 3. Streamflow and ground-water levels.

1940, and water-supply wells in the Kiser area along Miami Wash were abandoned in the late 1930's because of low pH. During 1940-86, acidic waste solutions at one mine were discarded in Webster Lake, an unlined reservoir with a capacity of about 5.5 x 10^6 cubic meters that formed when a tailings pile collapsed and dammed Webster Gulch (figs. 1 and 2). In February 1988 water at the lake surface had a pH of about 2.7 and contained 6,000 mg/L (milligrams per liter) of iron (Fe) and 20,000 mg/L of sulfate (SO_4). In 1986, the U.S. Environmental Protection Agency ordered the lake drained to eliminate it as a source of contamination (Arthur and Tolle, 1991, this Proceedings), and by May 1988 virtually all the lakewater had been spread on inactive tailings piles to evaporate. Other sources of contaminated water in the mined area have been described (Envirologic Systems, Inc., 1983), but the identification of specific sources has been impractical because of the duration of mining and the number of possible sources.

Acid-related contaminants have entered flowing streams in the basin during climatic wet cycles. Webster Lake last overflowed during February 1980, which resulted in total Fe concentration of 67 mg/L and pH of 5.7 on February 29, 1980, at Inspiration Dam. The estimated total load of Fe at the dam during the first half of 1980 was 450 Mg (megagrams). During the first half of 1985 the lake did not spill, but wet weather produced streamflow throughout the basin and brought ground-water levels close to stream-channel altitudes (fig. 3). Acidic ground water discharged into Miami Wash and its tributaries, beginning near well site 050 (fig. 1). Total Fe concentration at Inspiration Dam reached 45 mg/L, and the estimated load during 3 months was 266 Mg.

In the aquifer, acidic contaminated water mixes with uncontaminated ground water and reacts with calcite and other minerals to produce neutralized contaminated water from which most metals have precipitated (Eychaner, 1988, table 1). Neutralized contaminated water generally has pH greater than 6 and contains about 2,000 mg/L of SO_4 and 600 mg/L of calcium (Ca). Uncontaminated water contains less than 350 mg/L dissolved solids and reflects ground-water flow in contact with carbonate and silicate minerals.

The distribution of pH in the aquifer (fig. 4) depends on contaminant load, ground-water velocity, and the availability of reactive minerals. Walter and Norris (1991, this Proceedings) identified small-scale sedimentary features in the alluvium that correlate with pH. At site 050, 6 km downgradient from the former lake (fig. 4), water at the base of the alluvium has a pH of 3.6 and contains more than 1,000 mg/L of Fe, 5,000 mg/L of SO_4, and more than 100 mg/L of aluminum (Al) and copper (Cu). Variation in the water chemistry at site 050 was small during 1984-90. Near the base of the alluvium, pH increases gradually to about 5 near site 450, 15 km from the lake, and increases to about 6 near site 500, 2 km farther (fig. 4). All the alluvium and about 25 m of basin fill below it are contaminated with acidic or neutralized water.

The effect of reactions between aquifer material and acidic water is to retard the movement of many contaminants relative to the movement of the water itself (Eychaner, 1990). For example, the transition, or front, where Fe

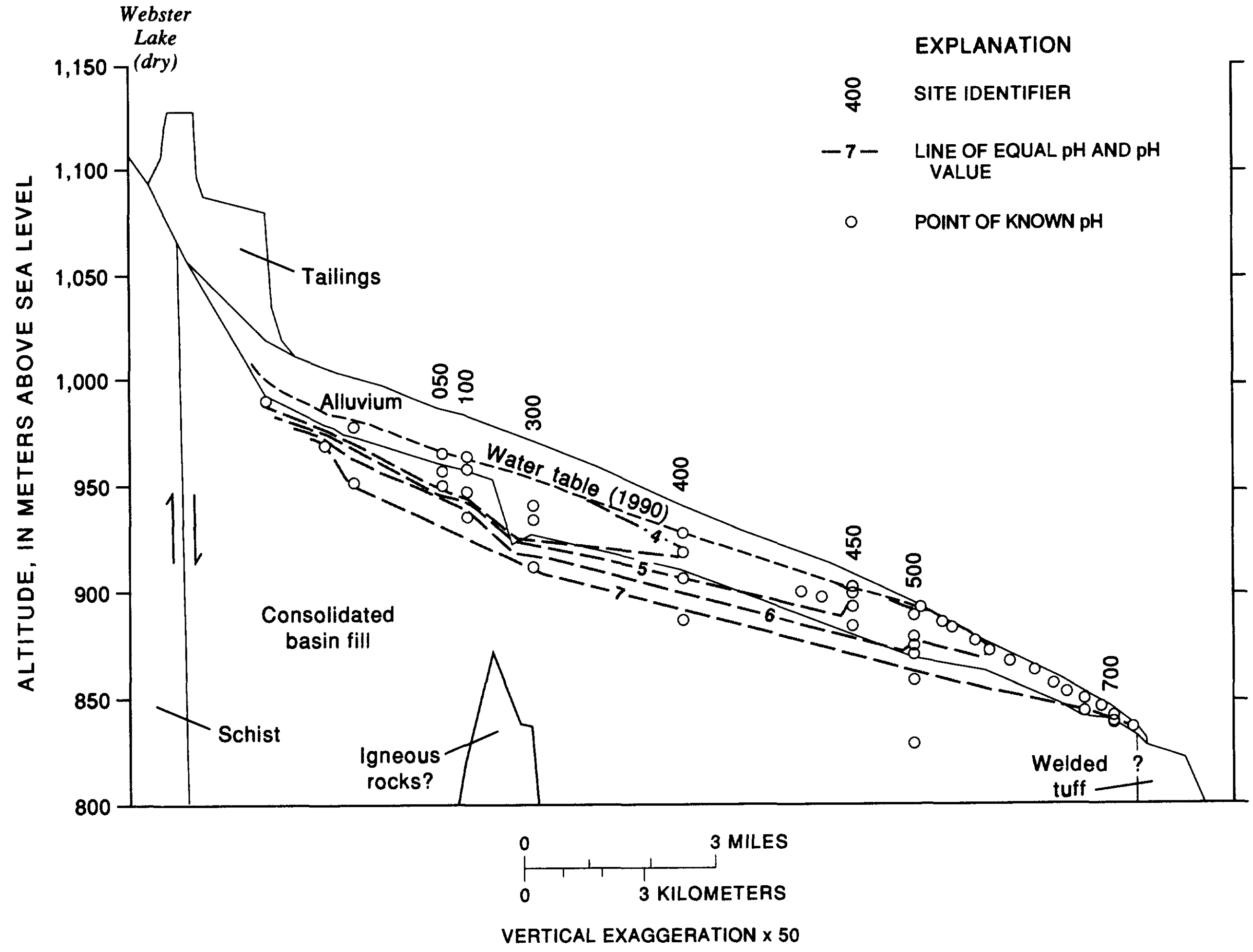
Webster Lake (dry)
1,150
1,100
1,050
1,000
950
900
850
800
ALTITUDE, IN METERS ABOVE SEA LEVEL
EXPLANATION
400 SITE IDENTIFIER
—7— LINE OF EQUAL pH AND pH VALUE
o POINT OF KNOWN pH
Tailings
Alluvium
050
100
300
400
450
500
700
Water table (1990)
4
5
6
7
Consolidated basin fill
Schist
Igneous rocks?
Welded tuff
?
0 3 MILES
0 3 KILOMETERS
VERTICAL EXAGGERATION x 50

Figure 4. Distribution of pH in the aquifer in 1990.

decreases from more than 100 mg/L to less than 1 mg/L is near site 450, and the distribution of Fe is closely related to pH. A front for each contaminant is determined by the interaction of its pH-dependent solubility, oxidation state, and ease of sorption on solid surfaces. The manganese (Mn) front moved past site 500 before 1984, but the Al front remained near site 400 in 1989.

A front of acidic water, at which pH falls below 5, has advanced through the alluvium at a rate of 0.2 to 0.3 km/yr (kilometers per year) during the past several decades. Between March 1989 and May 1990, the pH of water in two wells at site 450 decreased from 5.6 to 5.2 and from 4.9 to 4.3. The acid front moves most easily in zones of large hydraulic conductivity and small calcite content. A small part of the alluvial cross section is initially penetrated by the front, which expands laterally as the narrow finger moves downgradient (Hydro Geo Chem, 1989). If the acid front continued to advance at the historical rate, the 1.7 km from site 450 to the head of surface flow in March 1990 would be traversed in 5.7 to 8.5 years. Because the historical rate is based on average conditions across much of the alluvial section, however, an initial arrival could occur sooner.

In the 6-km reach of perennial streamflow upstream from Inspiration Dam (figs. 1 and 3), about a third of the inorganic carbon delivered by the ground water degasses as the water equilibrates with the atmosphere; resulting changes in dissolved carbonate species increase pH by about 2 units. Dissolved oxygen increases concurrently.

Dissolved-solids concentration at the dam increased from about 2,700 mg/L in 1980 to about 3,500 mg/L in 1989 despite temporary decreases during 1983-85 (Faires and Eychaner, 1991, this Proceedings, fig. 3). The concentration was about 800 mg/L in 1942 (Envirologic Systems, Inc., 1983, p. 6). Dilution calculations showed that uncontaminated water contributes less than 10 percent of base flow at the dam.

Dissolved Mn at Inspiration Dam increased from 0.5 mg/L in 1979 to about 35 mg/L during 1988-89 (Faires and Eychaner, 1991, this Proceedings, fig. 3). Estimated annual discharge of dissolved Mn at the dam was 20 Mg in 1980 and 200 Mg in 1989. More than 80 mg/L of Mn has been measured in streamflow upstream at Setka Ranch, but black Mn oxides precipitate on the streambed and decrease Mn concentration as pH and dissolved oxygen (O_2) increase. Visible accumulations of Mn were first observed in 1985, but streambed sediments provide only a temporary sink for Mn. As of 1990, intermittent sediment transport was a major, and largely unmeasured, process transporting metals out of the Pinal Creek basin. A median annual flood of 35 m^3/s could transport 10 to 50 Mg of Mn in a single day.

Because dissolved Mn increased at Inspiration Dam during a period of 10 years, each additional contaminant might begin to appear in streamflow as much as 5 years before reaching half its maximum concentration. At Setka Ranch, dissolved nickel (Ni) began to increase in 1988, followed by decreasing alkalinity and increasing dissolved Fe in 1989 (Faires and Eychaner, 1991, this Proceedings, fig. 4). At the dam 5 km downstream, however, no measurable changes in these constituents had occurred by late 1990.

A mining company has installed 17 monitoring and production wells in a reach 2 km long that spans the acid front in order to identify and capture water at pH less than 5 and to delay or prevent movement of the front. A major contaminant source has been eliminated by draining Webster Lake, and other wells near Miami Wash are being used to withdraw the most contaminated water. A large volume of low pH water is in transit through the aquifer, however, and several years will pass before the success of aquifer cleanup is assured.

RESEARCH IN PROGRESS

A broadly based research program is underway in the Pinal Creek basin and involves geochemical studies of ground and surface water, as well as collateral topics. Because hydraulics drives contaminant transport, Neaville (1989) designed a simulation model of ground-water flow in the alluvium and basin fill as it interacts with the surface drainage network. The model includes the whole aquifer; the principal inflows are mountain-front streams that recharge the aquifer, and the principal outflow is the perennial reach of Pinal Creek. Simulated ground-water traveltimes and pathlines from Webster Lake through the alluvium are consistent with historical, chemical, and hydraulic information (Brown, 1991, this Proceedings). Traveltimes to contaminated wells in the basin fill and the distribution of recharge, however, are inconsistent with some other evidence. Further study of mountain-front recharge patterns could help improve the model.

The principal geochemical controls in the Pinal Creek system are pH and oxidation-reduction potential (Eh). In ground water, pH is affected by reactions with carbonate minerals, by slower reactions with silicate minerals, and by production of hydrogen ions in metal-oxidation reactions (Stollenwerk and Eychaner, 1989). Within the framework of major acid-base and redox reactions, other elements are controlled by sorption, solid-solution mineral formation, or colloidal transport.

Many minerals have been identified in the alluvium. Carbonate minerals generally are present as coatings on and cement between silicate grains. In uncontaminated near-surface samples, Eychaner and Stollenwerk (1985) found 0.34 percent carbonate by weight. Ca concentrations in unsaturated-zone cuttings from well 010 indicate about 0.5 percent carbonate (Ficklin and others, 1991, this Proceedings). Following extensive drilling for remediation, Hydro Geo Chem, Inc. (1989) reported strong calcareous reactions in contaminated silt and clay zones north of well site 300 (fig. 1); the reactions were weaker in sands and larger sediments and absent south of well site 050 for all size fractions. Dispersed gypsum crystals, Fe-oxide coatings, and silicate minerals altered to clays are found in well cuttings from contaminated alluvium; Mn oxide coatings are present near former water-table elevations at some sites (Stollenwerk and Eychaner, 1989; Hydro Geo Chem, Inc., 1989; Ficklin and others, 1991, this Proceedings). Gypsum, Fe oxides, kaolinite, smectite, jarosite, silica, and particles containing Fe+Al+S were identified by scanning electron microscopy with energy-dispersive X-ray detection (SEM-EDX) on filters used in sampling for colloids at several sites (Puls and others, 1990). Several researchers have examined alluvial minerals using X-ray diffraction, but a complete list of identified minerals is not available.

Oxidation-reduction reactions principally involve Fe and Mn. Mn oxide coatings present in uncontaminated alluvium have been shown to be an effective oxidant of Fe^{2+} (Stollenwerk, 1991, this Proceedings; Glynn and others, 1991, this Proceedings). In column experiments isolated from atmospheric oxygen, Stollenwerk found a net loss of Mn from aquifer sediments while Fe precipitated.

Identification of the dominant terminal electron acceptors in the alluvium is uncertain, however, because about 7 mol (moles) of Fe precipitated in Stollenwerk's experiments for each mole of Mn that dissolved. Dissolved O_2 is less than 0.5 mg/L throughout the contaminated zone, and sufficient O_2 transport across the water table is unlikely. Although dissolved organic carbon (DOC) decreases concurrently with dissolved Al and Fe, the maximum measured DOC was only 4.2 mg/L (Wallin and others, 1991, this Proceedings). Finally, SO_4 reduction is possible, although thermodynamically unlikely. Wells at site 500 smell of hydrogren sulfide when initially opened for sampling, but the smell dissipates and no measurable concentration remains after purging. Reconnaissance samples show that a low population of SO_4-reducing bacteria is present in some wells.

Geochemical computer models have been used to simulate reaction paths and mass transport in the alluvium. On the basis of analyses with PHREEQE (Parkhurst and others, 1985), Fe concentrations appear to be in approximate equilibrium with amorphous $Fe(OH)_3$, although Fe^{3+} concentrations are too small to measure; platinum-electrode potentials measured in the field average about 0.12 volt smaller than would be expected at equilibrium (Stollenwerk and Eychaner, 1989). Al concentrations appear to be controlled by the solubility of microcrystalline gibbsite at pH greater than 4.7 and by dilution at lower pH (Stollenwerk and Eychaner, 1989). Novo-Gradac and Smith (1991, this Proceedings) modeled aqueous speciation of contaminants that have regulatory interest for the U.S. Environmental Protection Agency using MINTEQA2 (Allison and others, 1991).

Glynn and others (1991, this Proceedings) modeled simplified chemical mass transport in the ground water; they showed that calcite, dolomite, microcline, and birnessite (δ-MnO_2) dissolve from the aquifer and ferric hydroxide, gypsum, and gibbsite precipitate as the plume advances.

The dissolution of microcline is consistent with Stollenwerk's column experiment, which showed a gradual decrease in pH after the initial contaminant breakthrough (Stollenwerk and Eychaner, 1987). Gypsum in the aquifer is a solid-solution mineral containing about 0.2 percent impurities, but the thermodynamic equilibrium constant does not change significantly (Glynn, 1991, this Proceedings).

Sorption controls the distribution of cobalt (Co), Cu, and Ni in the ground water, and amorphous $Fe(OH)_3$ is the principal sorbent (Stollenwerk, 1990; 1991, this Proceedings). Thus the greatest sorption occurs in the same locations as the greatest Fe precipitation, and the process could be described as coprecipitation. Stollenwerk simulated sorption within the major reaction path by using the diffuse-layer surface-complexation model in MINTEQA2. Cu begins to sorb at a pH greater than 3.5, and at pH greater than 4.5 Co and Ni begin sorbing.

The formation and transport of inorganic colloids in a contaminated aquifer depends on the interaction of pH, mineral surface charge, ionic strength, and the dissolved constituents (Puls and others, 1991, this Proceedings). Substantial contaminant transport by colloids is possible, although the necessary combination of factors is unusual. Colloidal formation and transport near wells also is affected by pumping rate, purge time, and well construction. At well 451, pumping at 0.8 L/min (liters per minute) unexpectedly produced seven times more colloidal particles than pumping at 3.4 L/min; in the Pinal Creek area generally, particle concentrations took about 50 percent longer to stabilize in the field than O_2 or Eh and about twice as long as specific conductance, pH, or temperature (Puls and others, 1990).

As much as 4.2 mg/L of DOC is found in the aquifer, of which only about 0.5 mg/L represents uncontaminated background (Reese, 1989; Reese and Bassett, 1990). Organic contaminants include as much as 35 µg/L (micrograms per liter) of polycyclic aromatic hydrocarbons, which apparently sorb on Fe and Al hydroxides, and are most abundant where pH is less than 4.5 (Wallin and others, 1991, this Proceedings).

As the ground water becomes perennial streamflow in Pinal Creek, a different set of reactions predominates. Gas exchange with the atmosphere causes dissolved carbon dioxide (CO_2) to decrease and O_2 to increase downstream. Gas-transfer coefficients were measured in a 1-km reach using reaeration-measurement methods; the coefficients were 2.20/hr (per hour) for CO_2 and 2.46/hr for O_2 (Longsworth, 1991, this Proceedings). Mn oxide minerals precipitate in the perennial reach, and in the upper 60 mm (millimeters) of the streambed, about 13 Mg of Mn was measured per kilometer of channel (Haschenburger, 1989a). The minerals can be represented as rancieite ($(Mn_{0.85}Ca_{0.15})Mn_4O_9 \cdot 3H_2O$), although other minerals are present (Lind, 1991, this Proceedings). Determination of the controls on specific Mn oxide minerals and their sequence of formation is in progress. Abundant opportunities exist for reactions between streambed sediments and the shallow, turbulent streamflow in the perennial reach. Eychaner (1991, this Proceedings) developed a reaction-path model in PHREEQE to describe the evolution of pH, dissolved gases, and Mn along the reach. He estimated that about 0.9 mol of Ca dissolved from calcite for each mole of Mn that precipitated.

Trends in trace-metal concentrations in samples of the streamflow and adjacent shallow ground water were measured by inductively coupled plasma analysis with mass-spectrometric detection (Faires and Eychaner, 1991, this Proceedings). Concentrations of barium (Ba), cadmium (Cd), Co, and Ni decreased about 75 percent in a distance of 3 km, and metal concentrations as low as 2 µg/L were measured despite the high background of SO_4, Ca, and Mn. Sorption on streambed sediments, particularly Mn oxides, would keep dissolved concentrations of trace metals small (Stollenwerk, 1991, this Proceedings). For a 1.5-km reach downstream from Inspiration Dam, Cu concentrations in sediment fractions smaller than 0.125 mm were greater in samples from the streambed than from adjacent sedimentary bars, which implies a Cu source in the perennial flow (Haschenburger, 1989b).

In the perennial reach of Pinal Creek, biological processes could affect metal transport (Eychaner, 1991, this Proceedings). Limited biological observations began in March 1990, and additional work on algae in the streamflow is to continue during 1991.

Roosevelt Lake, which is a reservoir on the Salt River about 12 km downstream from Inspiration Dam, is the subject of a reconnaissance limnological study that began in late 1990. Goals of the study are to estimate elemental budgets in solution and on sediments from historical information, collect limited measurements of the full water column in the reservoir, and sample sediments to determine chemical availability at the water-sediment boundary.

SUMMARY

Water moving from an area of copper mining has contaminated an arid-zone aquifer and perennial stream and produced complex geochemical interactions among pH, mineral dissolution and precipitation, oxidation-reduction chemistry, and sorption near Globe, Ariz. Along Miami Wash and Pinal Creek, most of a band of unconsolidated alluvium 300 to 800 m wide and as much as 50 m thick is contaminated. Traveltimes from precipitation to outflow are less than 15 years for ground-water paths entirely within the alluvium, and average ground-water flow through the aquifer is about 0.27 m^3/s.

During dry climatic cycles, stream channels are ephemeral upstream from the perennial reach, but in wet cycles the aquifer fills and streamflow is continuous throughout the basin. Following a wet extreme, interrupted flow occurs for several months to a few years in areas of lower aquifer transmissivity. The beginning of perennial flow moved downstream about 600 m during 1988 and 1989.

The most contaminated water contains more than 1,000 mg/L of Fe, 5,000 mg/L of SO_4, and 100 mg/L of Al and Cu. A front at which pH falls below 5 has advanced through the alluvium at a rate of 0.2 to 0.3 km/yr during the past several decades and could arrive at the perennial reach of Pinal Creek within 6 to 8 years. Downgradient from the front and in stream base flow, neutralized contaminated water contains about 3,500 mg/L of dissolved solids, including about 2,100 mg/L of SO_4. Dissolved Mn in streamflow increased from 0.5 mg/L in 1979 to about 35 mg/L in 1988-89. At one streamflow-gaging station dissolved Ni began to increase in 1988 and alkalinity began to decrease in 1989, but no change has been measured at another station 5 km downstream. Aquifer cleanup began in 1987, but several years will pass before its success can be assured.

A broadly based research program is underway in the basin. The principal geochemical controls are pH and Eh. In ground water, pH is affected by reactions with carbonate minerals, by slower reactions with silicate minerals, and by production of hydrogen ions in metal-oxidation reactions. The alluvium contains about 0.4 percent carbonate, generally as coatings on and cement between silicate grains. Dispersed gypsum crystals, Fe-oxide coatings, and silicate minerals altered to clays are found in well cuttings from contaminated alluvium.

Mn oxide coatings present in uncontaminated alluvium are an effective oxidant of Fe^{2+}, but in column experiments about 7 mol of Fe precipitated for each mole of Mn that dissolved; identification of the dominant terminal electron acceptors is uncertain. A mass-transport model of the advancing plume simulated dissolution of calcite, dolomite, microcline, and Mn oxide from the aquifer and precipitation of ferric hydroxide, gypsum, and gibbsite. Sorption on ferric hydroxide controls the distribution of Co, Cu, and Ni.

As the ground water becomes perennial streamflow, gas exchange with the atmosphere causes CO_2 to decrease and O_2 to increase; Mn oxide minerals precipitate on the streambed. A reaction-path model simulated dissolution of about 0.9 mol of Ca from calcite for each mole of Mn that precipitated. Measured concentrations of Ba, Cd, Co, and Ni decreased about 75 percent in a distance of 3 km.

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PARTICLE-TRACKING ANALYSIS OF FLOW IN THE STREAM-AQUIFER SYSTEM IN PINAL CREEK BASIN, ARIZONA

By James G. Brown[1]

ABSTRACT

Acidic water has contaminated a stream-aquifer system near Globe, Arizona. A plume of contaminated ground water in alluvium and shallow basin fill along Miami Wash and Pinal Creek comes in part from an acidic lake that was drained in 1988. Simulated traveltimes from Webster Lake through the alluvium to Inspiration Dam were less than 15 years. The simulated traveltime from this lake to a well perforated in shallow basin fill exceeded 400 years. Inadequate simulation of individual pathlines in some areas may be the result of discretization effects, the use of inaccurate aquifer properties to represent basin fill, water-level fluctuations that result in downward movement of water, and(or) contaminants in the shallow basin fill that are present as a result of dispersive flow (which was not accounted for in the present analysis). Tritium concentrations indicate that water in the most contaminated part of the plume may be less than 20 years old.

INTRODUCTION

Acidic water has contaminated a stream-aquifer system near Globe Ariz. (fig. 1). The objectives of an ongoing study that began in 1984 (Eychaner, 1991) are to (1) study the movement and reactions of water and inorganic contaminants in the stream-aquifer system and (2) monitor the contamination. A mathematical flow model of the system was developed (C.C. Neaville, Hart Crowser, Inc., written commun., 1991) to improve our understanding of the regional flow system. This paper presents the results of a steady-state particle-tracking analysis of the time-averaged steady-state simulated flow system. Isotopic and chloride mass-balance analyses are included as comparative estimates of the mathematical model.

SIMULATION OF FLOW

The stream-aquifer system of the Pinal Creek drainage basin was simulated (C.C. Neaville, Hart Crowser, Inc., written commun., 1991) by using the modular three-dimensional finite-difference ground-water-flow model, MODFLOW (McDonald and Harbaugh, 1988). The basin was discretized into 49 rows, 28 columns, and 3 layers in a grid in which columns were aligned generally parallel with Pinal Creek. The model boundary in most places coincides with the aquifer boundary (fig. 1), except between Globe and the Pinal Mountains, where the model boundary is a ground-water divide. The upper layer (layer 1) consists of stream alluvium along Pinal Creek and Miami Wash, and basin fill from along the margins of these drainages to the edge of the model. Ground water is unconfined in the upper layer. The lower layers represent basin fill in which ground water is confined.

The aquifer is recharged mainly by streamflow infiltration in the upper reaches of ephemeral streams. In an underground mine near Globe, ground water flows into the basin fill from older, highly fractured subcrops. Ground water discharges to the northern part of Pinal Creek, where the aquifer is constricted laterally and at depth, and ground water returns to the surface (fig. 2). In addition, water is pumped from the aquifer and diverted from Pinal Creek about 2.5 km (kilometers) south of Inspiration Dam. Webster Lake contributed water to the aquifer from 1940 until it was drained in 1988. Chloride mass-balance analysis indicates that Webster Lake likely contributed 25 to 30 percent of the steady-state outflow at Inspiration Dam (Hydro Geo Chem, Inc., 1989).

Subsurface inflow at the underground mine, surface-water diversions, and ground-water pumping were simulated as specified, constant flows in the model. Stream-aquifer interactions were simulated by the streamflow routing package (Prudic, 1989), and inflow from Webster Lake was specified by a head-dependent flux boundary. A ground-water divide that extends from near Globe southward to the Pinal Mountains was modeled with a no-flow boundary. Elsewhere, low-permeability rocks form a barrier laterally, at depth, and downgradient, and are represented in the model by a no-flow boundary.

On the basis of Neaville's calibrated model, horizontal hydraulic conductivity ranged from 150 to 280 m/d (meters per day) in the alluvium and was 0.1 m/d in the basin fill. Specific yield of the alluvium was 0.1 in the southern part of the basin and 0.2 in the northern part; specific yield in the basin fill of layer 1 was 0.05, and the storage coefficient used in layers two and three was 0.0001 (C.C. Neaville, Hart Crowser, Inc., written commun., 1991).

PARTICLE-TRACKING ANALYSIS

The movement of ground water under time-averaged steady-state conditions was simulated by computer programs written by Pollock (1989) to compute pathlines and traveltimes of individual particles. Particle tracking requires the assignment of effective porosity to each active model cell. Specific-yield values from the model were used for porosity in initial simulations. Based on model porosity, simulated traveltime from Webster Lake to Inspiration Dam was 6 years. Traveltime was estimated to be from 4 to 14 years with simulated alluvium porosities of 0.1 to 0.4, respectively.

Particles were tracked backward from well sites 400 and 100 to determine ground-water source areas, traveltimes, and flow paths. Well 402 is perforated from 20 to 21 m (meters) below land surface in the lower part of the alluvium and yields water from the core of the plume (fig. 3). At well site 400 (fig. 1), ground water flows in the alluvium and uppermost basin fill parallel to the axis of the valley

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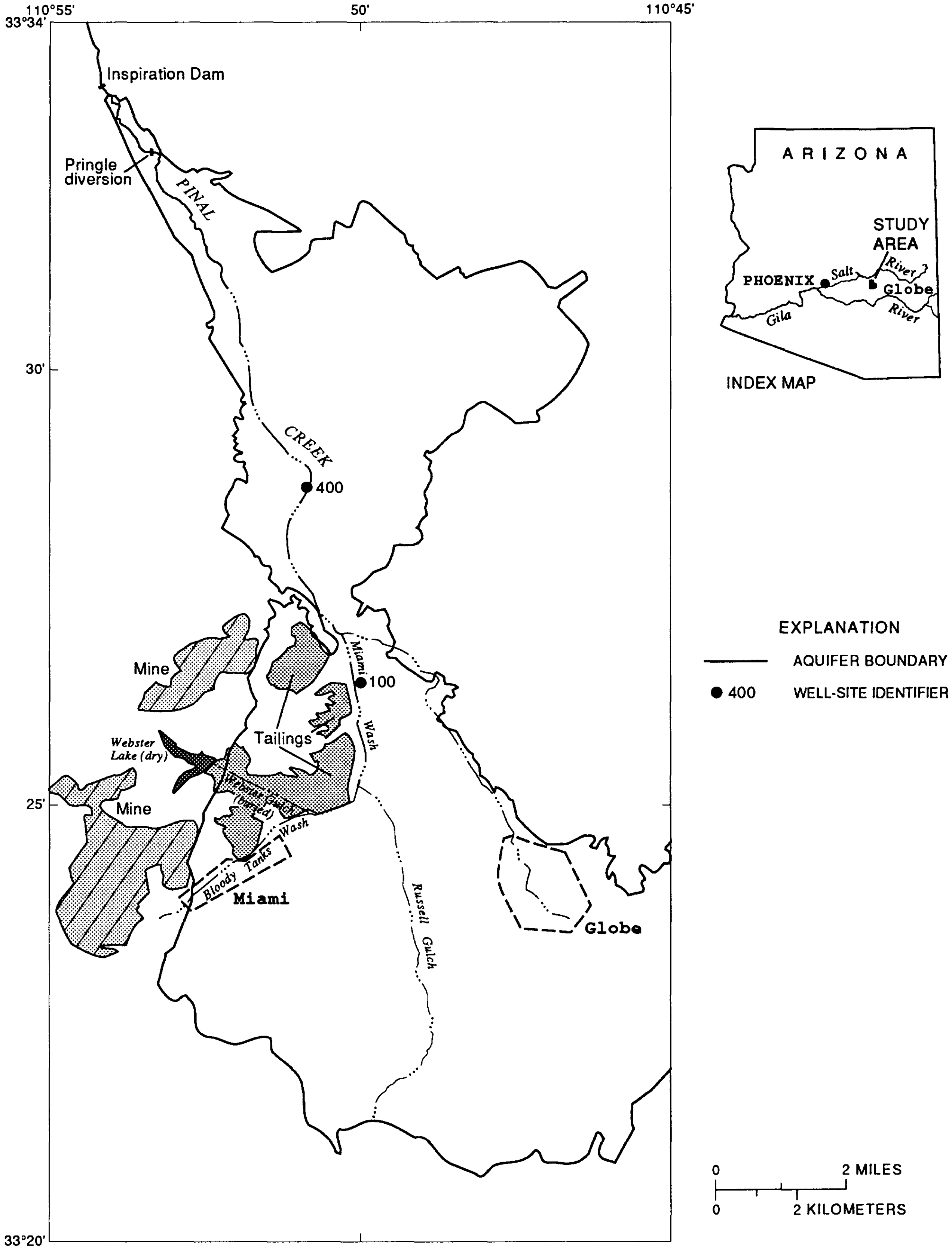
110°55'
50'
110°45'
33°34'
30'
25'
33°20'
Inspiration Dam
Pringle diversion
PINAL
CREEK
400
Mine
Miami Wash
100
Tailings
Webster Lake (dry)
Webster Gulch (buried)
Mine
Bloody Tanks Wash
Miami
Russell Gulch
Globe
ARIZONA
STUDY AREA
PHOENIX
Salt River
Globe
Gila River
INDEX MAP
EXPLANATION
AQUIFER BOUNDARY
● 400 WELL-SITE IDENTIFIER
0 2 MILES
0 2 KILOMETERS

Figure 1. Area of study.

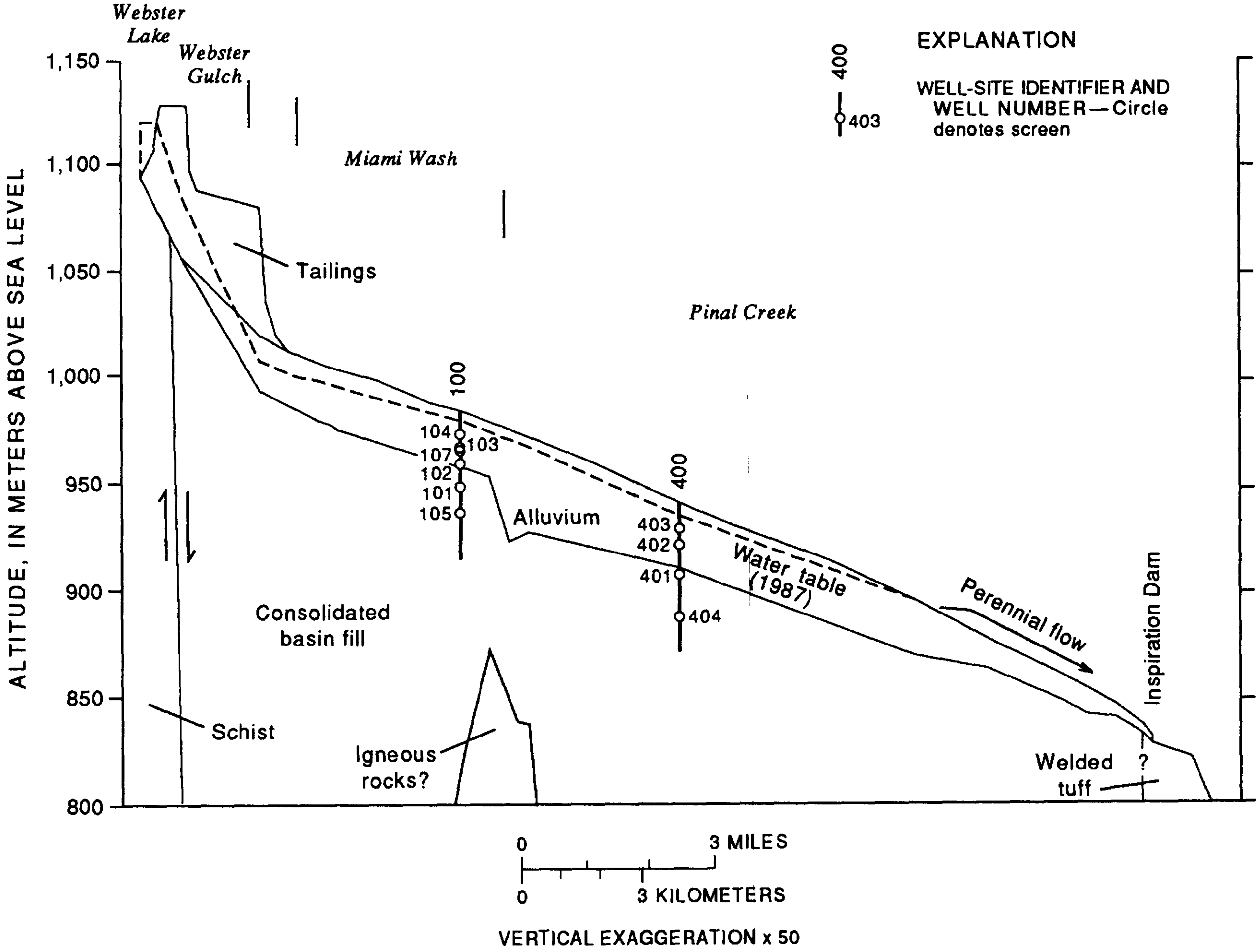
Webster Lake
Webster Gulch
Miami Wash
Tailings
Pinal Creek
EXPLANATION
400
403
WELL-SITE IDENTIFIER AND WELL NUMBER—Circle denotes screen
ALTITUDE, IN METERS ABOVE SEA LEVEL
1,150
1,100
1,050
1,000
950
900
850
800
100
104
107
103
102
101
105
Alluvium
400
403
402
401
404
Water table (1987)
Perennial flow
Inspiration Dam
Consolidated basin fill
Schist
Igneous rocks?
Welded tuff
?
0
3 MILES
0
3 KILOMETERS
VERTICAL EXAGGERATION x 50

Figure 2. Generalized geologic section of the aquifer.

(fig. 4). To assess this flow qualitatively, 24 particles were arranged vertically for 10 m and laterally for 200 m. Eighteen pathlines that were tracked backwards from well 402 originated in the Pinal Mountains, four originated in Webster Lake, and one originated from the underground mine near Globe (figs. 4 and 5). Simulated traveltime from Webster Lake to well 402 through the alluvium was 4 to 5 years, whereas simulated traveltime from recharge in the Pinal Mountains through basin fill to well 402 ranged from about 300 to about 700 years. From well 404, which is perforated from 54 to 55 m below land surface in uncontaminated basin fill, all particles were tracked backward to the recharge area to the east; simulated traveltimes were about 600 years.

Well 101 is perforated in contaminated basin fill about 10 m below the base of the alluvium (fig. 2). Particles were tracked back from well 101 to both Webster Lake and Pinal Mountains. Particles that were tracked back to Webster Lake traveled deep through basin fill with traveltimes of about 600 years. Webster Lake, however, was formed in 1940 and large-scale mining began near Webster Gulch around 1910, indicating that the simulated traveltimes are too long.

The model does not appear to simulate flow from Webster Lake to well 101 (in shallow basin fill) adequately because (1) the present degree of discretization, although adequate for simulation of bulk ground-water flow, may be inadequate to reliably simulate pathlines in places where aquifer properties differ significantly over the volume represented by a model cell (which uses an average value throughout); (2) basin-fill horizontal hydraulic-conductivities values, which were estimated from sparse data, may be inaccurate; (3) contamination in shallow basin fill is caused, at least in part, by dispersive flow; and(or) (4) water-level fluctuations may cause a downward movement of water (and contaminants).

Tritium concentrations were used as qualitative indicators of ground-water age. Contaminated water contained 9.5 to 86 pCi/L (picocuries per liter) of tritium, indicating that the water included some precipitation that fell later than 1953, when atmospheric testing of thermonuclear bombs began. Tritium concentrations in the most contaminated part of the plume ranged from 26 to 47 pCi/L, indicating that ground water would still contain water that entered the aquifer between 1970 and 1981, even if diluted 2:1 by water that fell as precipitation prior to 1953.

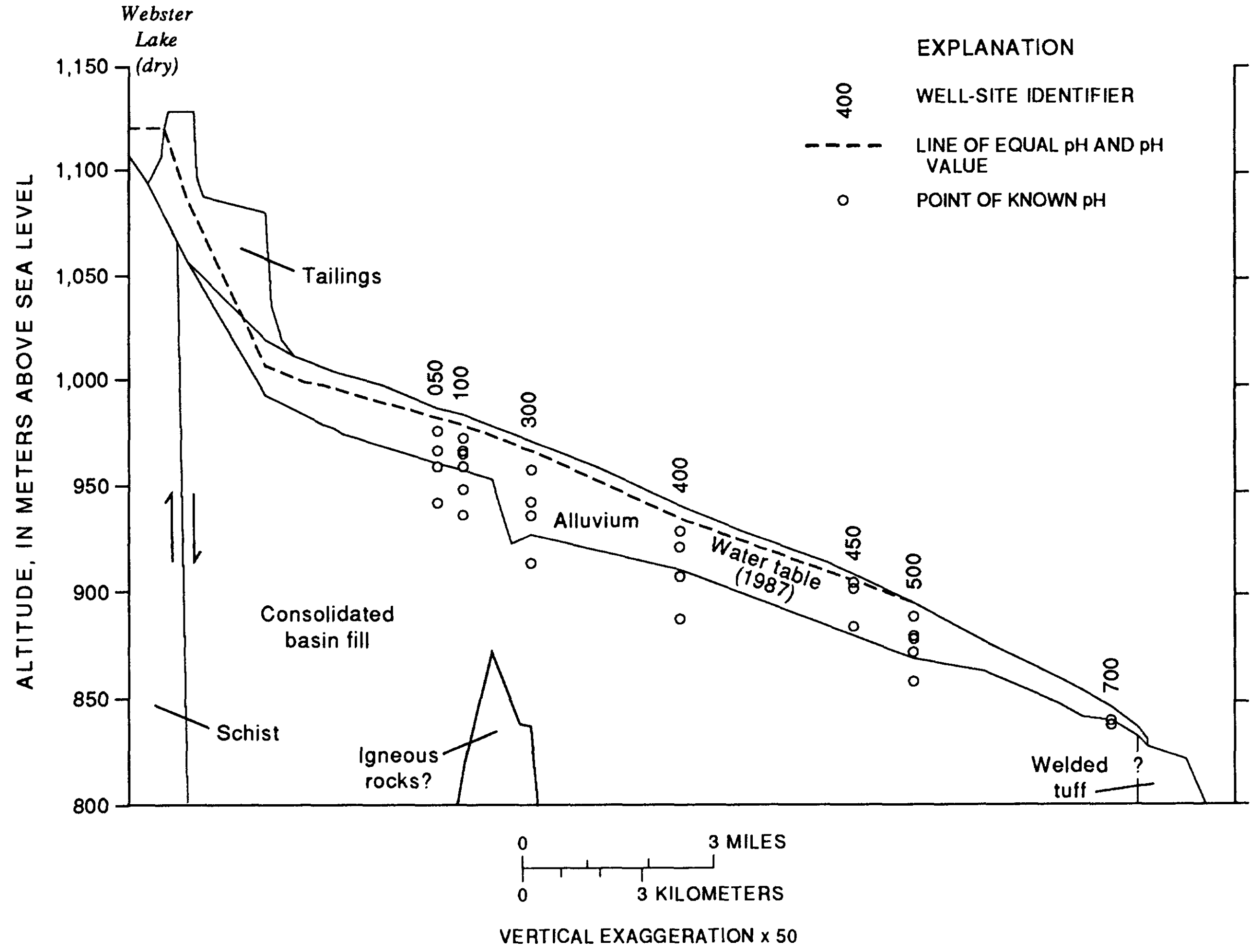
Webster Lake (dry)
EXPLANATION
400 WELL-SITE IDENTIFIER
LINE OF EQUAL pH AND pH VALUE
o POINT OF KNOWN pH
ALTITUDE, IN METERS ABOVE SEA LEVEL
1,150
1,100
1,050
1,000
950
900
850
800
Tailings
050
100
300
400
450
500
700
Alluvium
Water table (1987)
Consolidated basin fill
Schist
Igneous rocks?
Welded tuff
?
0
3 MILES
0
3 KILOMETERS
VERTICAL EXAGGERATION x 50

Figure 3. Distribution of pH in the aquifer, 1990.

Uncontaminated water from basin fill at sites 400 and 500 contained less than 0.1 pCi/L of tritium, indicating that most of the water from these wells was recharged before 1953. These ages are consistent with traveltimes calculated from the flow model along three flowlines: (1) from Webster Lake through the alluvium to Inspiration Dam, (2) to wells perforated in uncontaminated basin fill below the plume, and (3) to a well in contaminated alluvium. The more than 200-year traveltime from Webster Lake to a well perforated in shallow basin fill is longer than that indicated on the basis of tritium concentrations.

CONCLUSIONS

Simulated ground-water traveltimes and pathlines from Webster Lake through the alluvium are consistent with historical, chemical, and hydraulic information. Simulated traveltimes from Webster Lake through the alluvium to Inspiration Dam were less than 15 years. The simulated traveltime from Webster Lake to a well perforated in contaminated basin fill was over 400 years, indicating that the model may not reasonably simulate individual pathlines in shallow basin fill. The apparent discrepancy may be related to discretization effects, the use of inaccurate aquifer properties to represent basin fill, water-level fluctuations that result in downward movement of water (and contaminants), or contaminants in the shallow basin fill that are present as a result of dispersive flow (which was not accounted for in the present analysis). Tritium concentrations indicate that much of the contaminated water could be less than 20 years old.

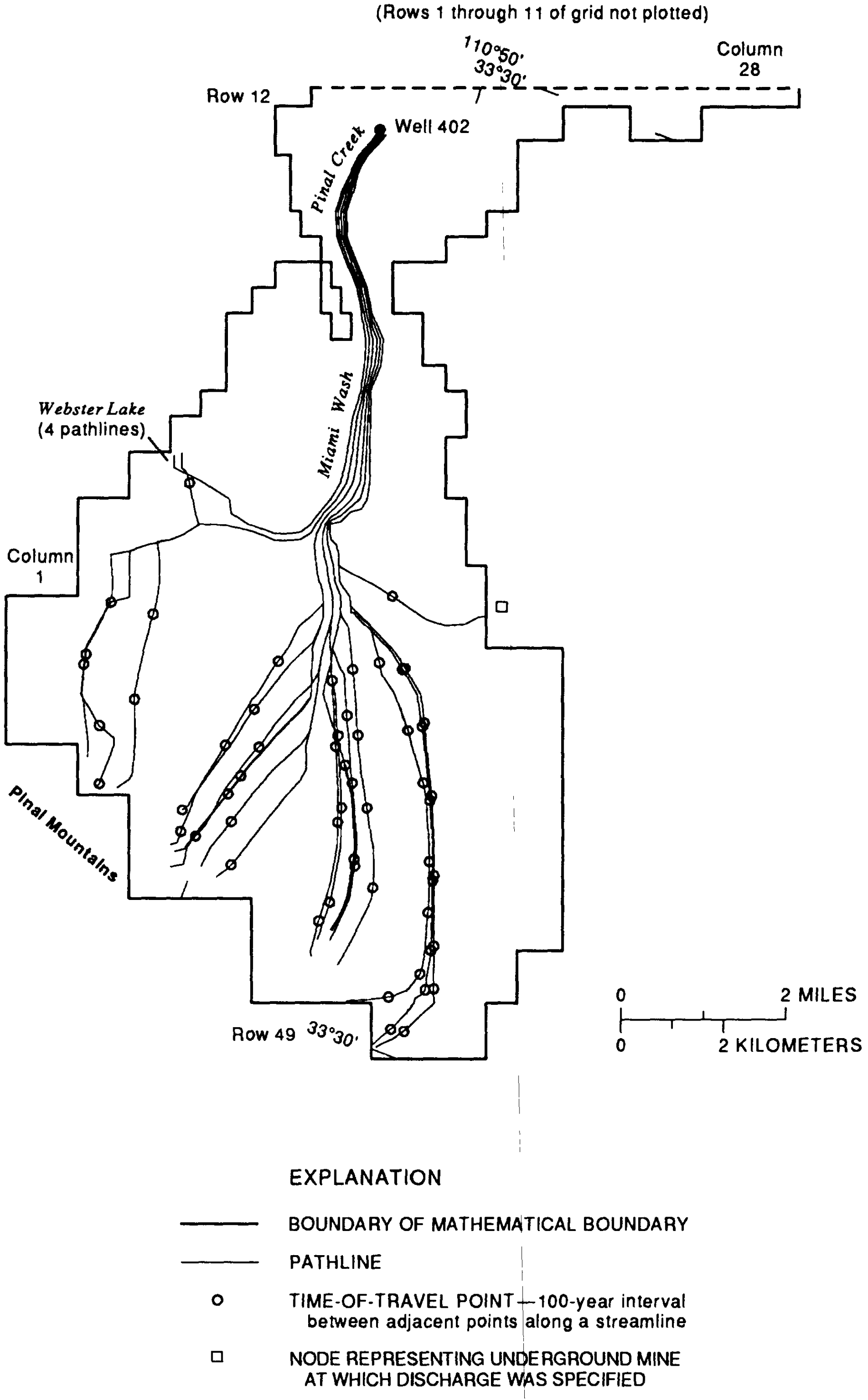
(Rows 1 through 11 of grid not plotted)
110°50'
33°30'
Column 28
Row 12
Well 402
Pinal Creek
Miami Wash
Webster Lake (4 pathlines)
Column 1
Pinal Mountains
Row 49
33°30'
0
2 MILES
0
2 KILOMETERS
EXPLANATION
BOUNDARY OF MATHEMATICAL BOUNDARY
PATHLINE
o TIME-OF-TRAVEL POINT—100-year interval between adjacent points along a streamline
□ NODE REPRESENTING UNDERGROUND MINE AT WHICH DISCHARGE WAS SPECIFIED

Figure 4. Pathlines and time-of-travel points tracked backwards from well 402.

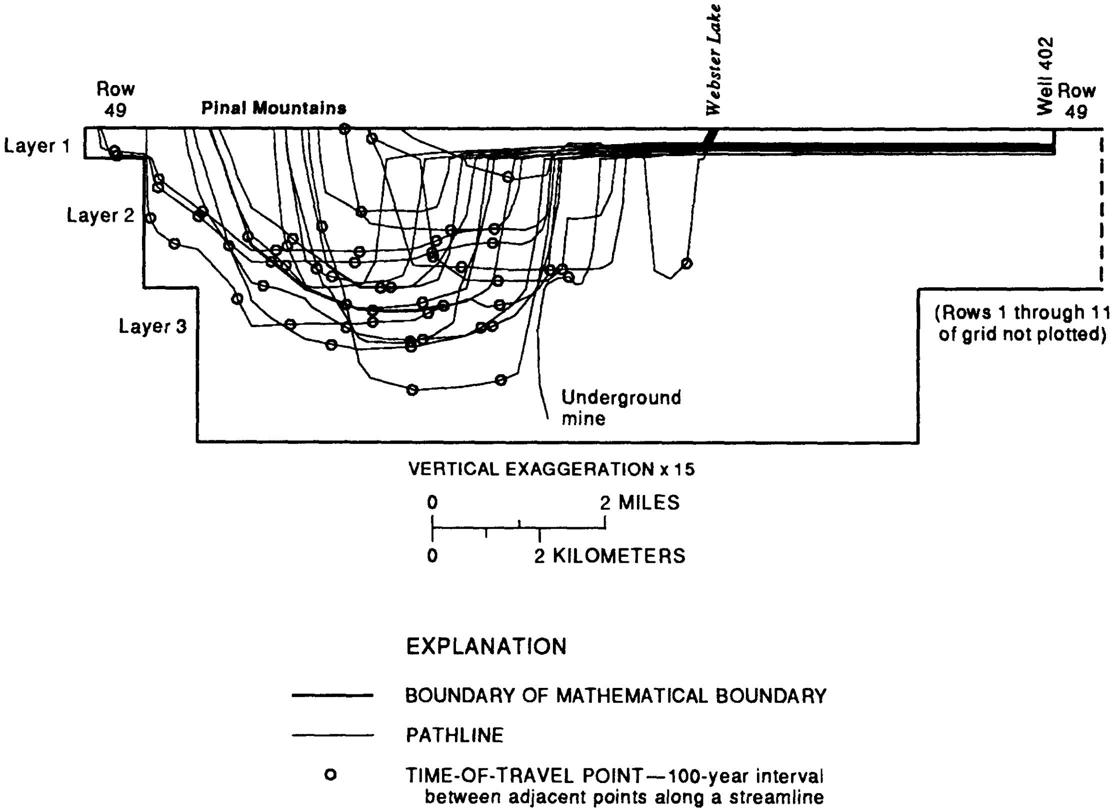
Row 49
Pinal Mountains
Webster Lake
Well 402
Row 49
Layer 1
Layer 2
Layer 3
(Rows 1 through 11 of grid not plotted)
Underground mine
VERTICAL EXAGGERATION x 15
0
2 MILES
0
2 KILOMETERS
EXPLANATION
BOUNDARY OF MATHEMATICAL BOUNDARY
PATHLINE
TIME-OF-TRAVEL POINT—100-year interval between adjacent points along a streamline

Figure 5. Cross section showing pathlines and time-of-travel points tracked backwards from well 402 (projected to column 17).

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USE AND LIMITATIONS OF TWO COMPUTER CODES FOR SIMULATING GEOCHEMICAL MASS TRANSPORT AT THE PINAL CREEK TOXIC-WASTE SITE

By Pierre D. Glynn[1], Peter Engesgaard[2], *and* Kenneth L. Kipp[3]

ABSTRACT

The chemical evolution of acidic contaminated water at the Pinal Creek, Arizona, toxic-waste site cannot be realistically simulated by current contaminant-transport computer codes. The Pinal Creek site serves as an example of the capabilities and limitatations of PHREEQM and MST1D, two computer codes capable of simulating the transport of contaminants affected by aqueous-speciation and mineral dissolution/precipitation processes as well as by the physical processes of advection and dispersion. The results of the PHREEQM and MST1D simulations are remarkably similar, given the difference in their numerical algorithms.

INTRODUCTION

Most currently available contaminant-transport codes are incapable of describing common chemical reactions, such as the dissolution/precipitation of minerals and dissolution/exsolution of gases. As a result, few computer codes can be used to simulate the chemical evolution of acid and heavy-metal contaminated ground waters, such as those found at the Pinal Creek, Ariz., toxic-waste site. At the Pinal Creek site, the transport of most contaminants is strongly dependent on the pH and pe^- conditions of the ground waters. In turn, pH and pe^- are determined by, and are also the result of, reaction processes such as, (1) the dissolution of carbonate and silicate minerals; (2) the oxidation of aqueous Fe(II) and reduction of Mn(IV), which results in the precipitation of $Fe(OH)_3$ and dissolution of bimessite (MnO_2); and (3) the exsolution of CO_2 gas and the dissolution of O_2 gas. Many other reaction processes also affect the transport of contaminants. For example, 50 percent of the aqueous Fe(II) and Mn (II) are in the form of sulfate ion pairs. Similarly, sulfate ion pairs could also be dominant complexes for other heavy metals. As a result, sulfate, a rather innocuous contaminant in itself, could significantly contribute to the transport of metals at Pinal Creek. Because sulfate ion pairs/complexes with divalent metals will form relatively large ions of neutral charge, adsorption and(or) ion exchange will not offer significant retardation of these particular complexes. Thus, sulfate control through the precipitation of gypsum is an important process, although it is only one of many reactions to be considered in any attempt to simulate the transport of contaminants at Pinal Creek realistically.

Few contaminant-transport codes have been developed that are capable of simulating the complex chemical processes outlined above in addition to the physical processes of advection and dispersion. Several types of contaminant-transport codes are capable of simulating multiple, heterogeneous, chemical reactions: (1) mixing-cell models (for example, PHREEQM) (Appelo and Willemsen, 1987; Appelo and others, 1990) (2) sequential-iteration models (for example, MST1D), (Engesgaard, 1989; 1991; P.A. Engesgaard, Technical University of Denmark, and K.L. Kipp, U.S. Geological Survey, written commun., 1991); and (3) mixed-differential algebraic models (for example, CHMTRNS), (Noorishad and others, 1987). The objective of these models is to solve a set of partial-differential equations describing the physical processes of advection and dispersion, together with a set of nonlinear algebraic equations describing chemical mass transfer and aqueous speciation. MST1D iterates sequentially between solving the partial-differential equations of transport by an implicit finite-difference method and running the geochemical mass-transfer code PHREEQE (Parkhurst and others, 1990) to solve the set of algebraic equations. In contrast, mixed-differential-algebraic models, such as CHMTRNS, attempt to solve the entire set of differential and algebraic equations simultaneously in a single matrix equation. Because of their finite-difference formulation of the advection-dispersion equations, both the CHMTRNS and MST1D algorithms could be extended into two-dimensional and three-dimensional transport codes. In contrast, the mixing-cell model PHREEQM (which adds transport subroutines to the PHREEQE code) does not depend on a combined numerical formulation of the advection-dispersion equation. Instead, the processes of advection and dispersion are simulated in separate steps. In the PHREEQM code, a simulation column is subdivided into a series of "cell volumes." The advection process is modeled by "shifting" the entire contents of each cell volume into the next volume at each time step. The ground-water velocity is specified by choosing an appropriate cell length and time step; these two variables cannot be chosen independently of each other. The dispersion process is modeled by mixing the contents of each cell with that of its adjacent cells. The mixing factors f calculated are a function of both aquifer dispersivity α and molecular diffusion D^*:

$$f_i = \frac{\alpha_i + \alpha_{i+1}}{l_i + l_{i+1}} + 4D^* \frac{dt}{(l_i + l_{i+1})^2} \quad ,$$

where l_i is the length of cell i and dt is the time step. Chemical equilibration of each cell (with the PHREEQE code) occurs between the advection and dispersion steps. No sequential iterations are performed between the chemical equilibration, advection, and dispersion steps.

Model validation and comparison is an important prerequisite in using contaminant-transport models with complex chemistry and should help in both understanding the limitations of these models and in gaining confidence in their actual capabilities. This paper is a first attempt to examine the capabilities and limitations of PHREEQM and MST1D in simulating the evolution of acid-contaminated ground waters, such as found at the Pinal Creek site. Our attempts at using the CHMTRNS code were unsuccessful, mainly because of excessive computer time requirements. The CHMTRNS code is, therefore, not considered in this comparison.

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PROBLEM DESCRIPTION

The hydrogeologic setting of the Pinal Creek toxic-waste site has been described previously by Eychaner (1989). Contaminant transport at the site occurs for the most part in a phreatic aquifer, composed of unconsolidated alluvial deposits. An indurated alluvial conglomerate, the Gila Conglomerate, underlies this upper aquifer and has also been partly contaminated, but not to the extent of the upper alluvial aquifer. Our problem objective is to simulate the flow and transport of acidic wastewater and its major constituents, for 50 days, along a 300-m (meter) stretch of the Pinal Creek alluvial aquifer. Average ground-water velocity is 5 m/d (meters per day), as reported by Eychaner (1989). For the purpose of our modeling exercise, ground-water flow in the aquifer is assumed to be in steady-state. Dispersivity is assumed constant at 5 m and aquifer porosity at 0.3.

Uncontaminated ground water at the Pinal Creek toxic-waste site has the following typical composition (results represent well 010 and are in moles per kilogram of H_2O): pH = 6.91, $pe^- = 11.0$, $Ca = 1.37 \times 10^{-3}$, $Cl = 5.08 \times 10^{-4}$, $Sr = 4.22 \times 10^{-6}$, $Mg = 8.64 \times 10^{-4}$, $Na = 1.17 \times 10^{-3}$, $M = 5.46 \times 10^{-7}$, $SO_4 = 7.08 \times 10^{-4}$, $SiO_2 = 4.49 \times 10^{-4}$, Total dissolved inorganic carbon (TDIC) = 4.06×10^{-3}, $Fe = 7.16 \times 10^{-7}$, $Al = 1.85 \times 10^{-5}$. A negatively charged monovalent component m_1^- is added to obtain electrical balance of the speciated water: $M_1^- = 4.584 \times 10^{-4}$.

The aquifer water is assumed to be initially at equilibrium with the following minerals (with amounts in the aquifer expressed as moles per kilogram of H_2O): calcite (4.20×10^{-2}), dolomite (2.10×10^{-2}), soil CO_2 gas ($P_{CO_2} = 10^{-2}$, infinite reservoir), microcline (1.75×10^{-2}), birnessite (2.00×10^{-2}). In addition, the following minerals, which are not initially present, are allowed to precipitate to equilibrium upon condition of supersaturation: $Fe(OH)_3$, gypsum, silica gel, gibbsite.

The wastewater has the following composition (representative of well 51 at the Pinal Creek site): pH = 3.74, $pe^- = 6.00$, $Ca = 1.10 \times 10^{-2}$, $Cl = 9.59 \times 10^{-3}$, $Sr = 1.48 \times 10^{-5}$, $Mg = 1.60 \times 10^{-2}$, $Na = 9.13 \times 10^{-3}$, $Mn = 1.37 \times 10^{-3}$, $SO_4 = 9.16 \times 10^{-2}$, $SiO_2 = 1.66 \times 10^{-3}$, $TDIC = 4.16 \times 10^{-3}$, $Fe = 5.01 \times 10^{-2}$, $Al = 9.27 \times 10^{-3}$. To maintain charge balance, component $M_1^- = 1.6376 \times 10^{-3}$ is added to this inflowing water.

During the simulation and also in the initial equilibration steps of the inflowing and background waters, pH and pe^- are allowed to vary.

Many components, such as Cu, Ni, Cd, Zn, Cr, present in the contaminated ground water at Pinal Creek, are ignored partly for the sake of simplicity, partly because of their absence from the original PHREEQE data base[4]. The aquifer water is assumed not to receive any input of atmospheric oxygen (the only other option, complete equilibration with atmospheric oxygen, would have been unrealistic). Although PHREEQM has the capability of simulating a constant input/output of a reactant (such as oxygen) for a given number of cells and time steps, MST1D does not currently have that capability. Similarly, ion exchange processes, which can be simulated in PHREEQM but not in MST1D, are ignored. The current versions of PHREEQM and MST1D also cannot simulate adsorption or solid-solution precipitation/recrystallization processes. Finally, both simulations use the local equilibrium assumption, which postulates that the rate of reaction of any component (or species) per unit cell volume is much faster than the advective-dispersive flux of the component through the given cell volume. PHREEQM and MST1D are used as equilibirum models with no specification of reaction kinetics. Bahr (1990) gives an excellent discussion of the conditions of applicability of the local equilibrium assumption to contaminant transport affected by both heterogeneous and homogeneous chemical reactions.

SIMULATION RESULTS

The PHREEQE thermodynamic data base used in both programs was identical. Although some modifications were made to the PHREEQE subroutines in MST1D in order to speed up the code, differences in the results obtained by MST1D and PHREEQM should be caused only by the differences in the numerical algorithms used to simulate advection and dispersion and by the lack of sequential iterations between transport and chemistry in PHREEQM.

The PHREEQM simulation was conducted on a Prime[5] 6550 minicomputer, rated at 11.7 MIPS (million instructions per second) by Prime Inc. and running PRIMOS rev. 21. A cell length of 5 m was used, with an ensuing time step of 1 day (in order to obtain the average linear velocity of 5 m/d typical of the Pinal Creek). A CPU time of 97 minutes was required to run the simulation. Several runs were also made with a cell length discretization of 10 m. The CPU time required for those runs was approximately 13 minutes.

The MST1D simulation was conducted on a Hewlett-Packard 9000 model 375 workstation, rated by Hewlett-Packard at 7 MIPS and 0.5 MFLOPS (million floating point operations per second). The initial simulation used a discretization (dx) of 10 m and a maximum time step (dt) of 2 days. Under those conditions, the CPU time required was approximately 2 hours on the workstation. Significant numerical dispersion was found in the model results, however, and the simulation was repeated with a discretization of 5 m and a maximum time-step increment of 0.1 days. This second simulation was conducted after an upgrade of the Hewlett-Packard workstation to 12 MIPS and runtime was approximately 21 hours.

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[4] A new version of PHREEQE (Parkhurst and others, 1990 revision) with a revised and slightly expanded data base is now available, but PHREEQM and MST1D have not yet been converted to use it.

[5] Use of brand, firm, or names in this paper is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

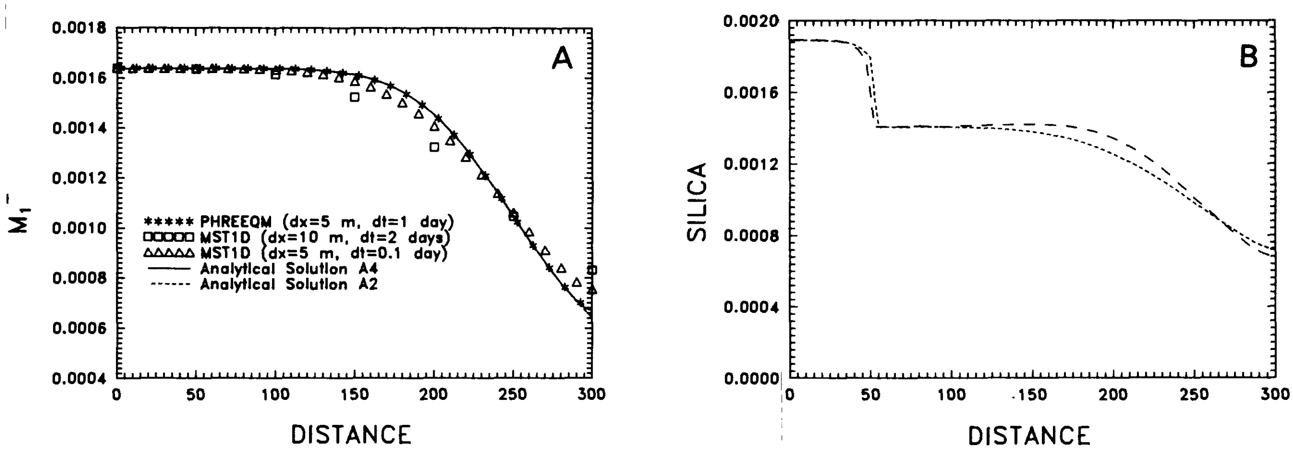

Figure 1. (A)Spatial profiles of conservative contaminant m_1^- at 50 days; compairson of MST1D and PHREEQM results with analytical solutions. (B) Spatial profile of total dissolved silica at 50 days. The dotted and dashed lines represent the MST1D and PHREEQM results, respectively, in moles per kilogram of H_2O.

Results of the MST1D and PHREEQM simulations of transport of conservative constituent M_1^- are given in figure 1A, together with analytical solutions A2 and A4 of Van Genuchten and Alves (1982). Solutions A2 and A4 are solutions to the one-dimensional advection-dispersion equation, with a third-type boundary condition (continuity of contaminant flux) at the inflow and a second-type boundary-condition (no dispersive flux) at the outflow. Although solution A2 is applicable to the case of a semi-infinite column, whereas solution A4 is for a fixed-length column, both solutions give identical results at 50 days except in the last 5 m of the simulation column. Although PHREEQM perfectly matches the analytical solutions (fig. 1A), MST1D has some numerical dispersion problems that can be significantly reduced by choosing a smaller grid spacing and a smaller maximum time step. In the initial MST1D run with dx = 10 m and dt = 2 days, the dispersion observed in the transport of constituent m_1^- was more than twice the specified physical dispersion. The results of the second MST1D run are much closer to the analytical solution, but still show some numerical dispersion, relative to PHREEQM and to the analytical solution results. This can be best seen in the spatial profile of H_4SiO_4 (fig. 1B), which is almost conservative if one excludes the initial dip at approximately 50 m caused by the increase in pH.

Spatial profiles of several nonconservative aqueous components after 50 days of model simulation are shown in figures 2 and 3. Corresponding mineral profiles are also given. The results given by PHREEQM and MST1D (run #2) are remarkably similar, given the disparity in the numerical algorithms used by the two codes. Nevertheless, there is an offset in some of the aqueous-concentration fronts and in some of the mineral-abundance fronts. The PHREEQM fronts consistently lag behind the MST1D fronts. The offset is usually smaller than the 5-m resolution used by the PHREEQM simulation, but reaches a maximum of 7.5 m at specific front concentrations. Because MST1D, unlike PHREEQM, iterates between the chemical equilibration and transport steps, the front positions given by MST1D are expected to be more accurate than those determined by the PHREEQM code. This is only true, of course, if numerical dispersion in the MST1D results is kept negligible by choosing a small enough time step and grid spacing. Decreasing the time step and grid spacing may also result in a smaller number of sequential iterations, however. In the MST1D simulation shown in figures 2 and 3, (maximum dt = 0.1 days, dx = 5 m), the number of sequential iterations at each time step varied from 10 to 15, with an average of 12. In the earlier MST1D simulation with a coarser discretization, the number of sequential iterations at specific times was as large as 60. Engesgaard and Kipp (P.A. Engesgaard, Technical University of Denmark, and K.L. Kipp, U.S. Geological Survey, written commun., 1991) investigated the effect of sequential iterations and time step reduction on the accuracy of mineral-front positions. In their study example, based on a denitrification reaction by oxidation of pyrite, removing sequential iterations created a large shift in front positions. Decreasing the time step by a factor of 5 (which was approximately the number of sequential iterations used) was computationally much less efficient than keeping the sequential iteration option.

Numerical dispersion is partly responsible for the offset in front positions. Greater dispersion causes an earlier arrival of contaminant solution at a particular position in the simulation column and is, therefore, responsible for the earlier depletion of initially present reactant minerals, such as calcite, dolomite, and birnessite. As a result, the effect of greater dispersion is to move the contaminant fronts farther along the column after a fixed length of time. This effect partly explains the offset between the PHREEQM and MST1D fronts. The offset between the fronts of the initial MST1D run (with dx = 10 m and dt = 2 days) and those given by PHREEQM was approximately two times greater than the offset present in the second MST1D run.

Finally, part of the lag between the PHREEQM and MST1D simulations is the result of discretization error. Although MST1D gives concentrations at node positions,

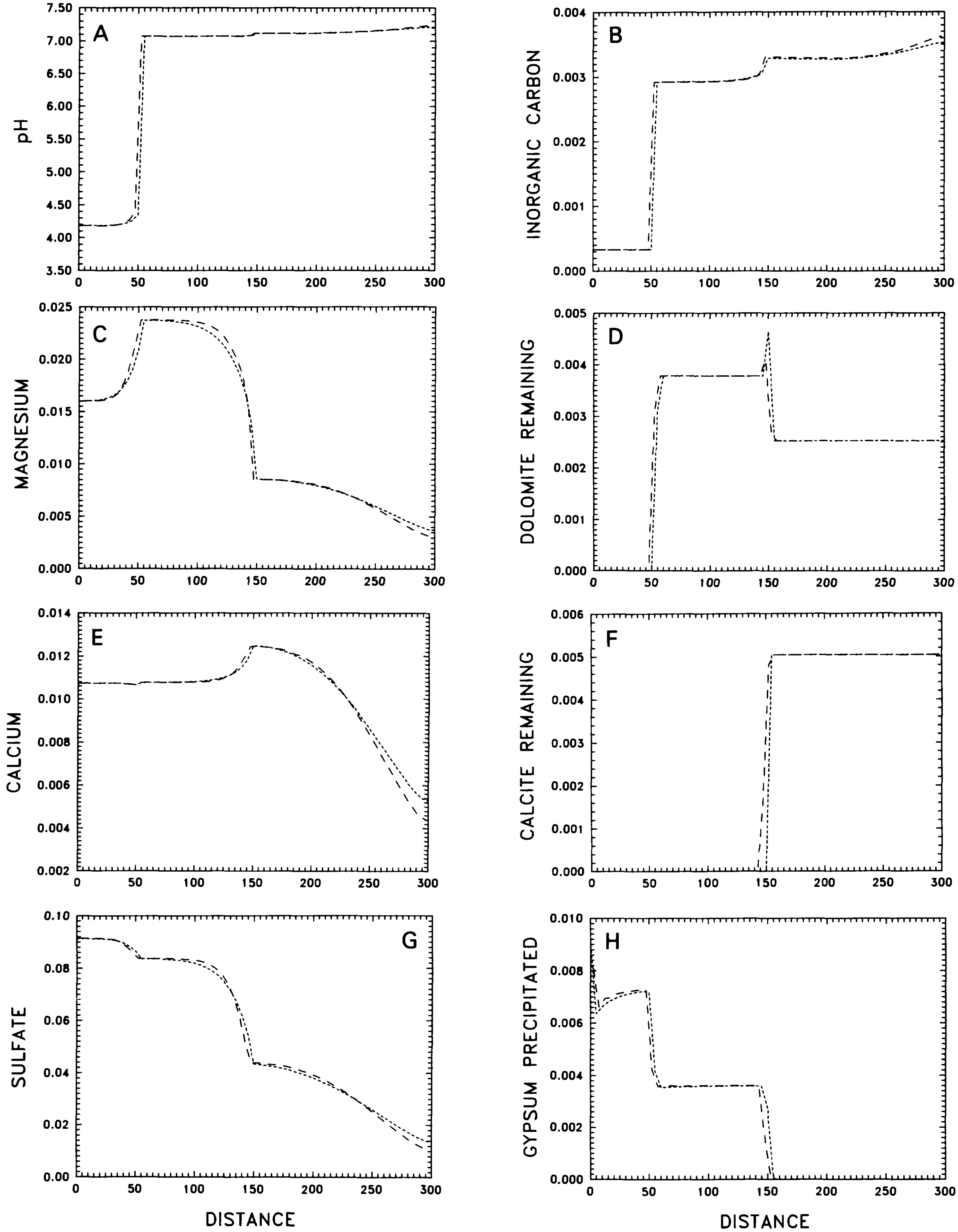

Figure 2. (A-H) Spatial profiles at 50 days of various pH-dependent total aqueous-concentrations and mineral amounts. The dotted and dashed lines represent the MST1D and PHREEQM results, respectively, in moles per kilogram of H_2O for aqueous concentrations, and in moles per kilogram of solid (bulk density = 2,500 kilograms per cubic meter) for mineral concentrations.

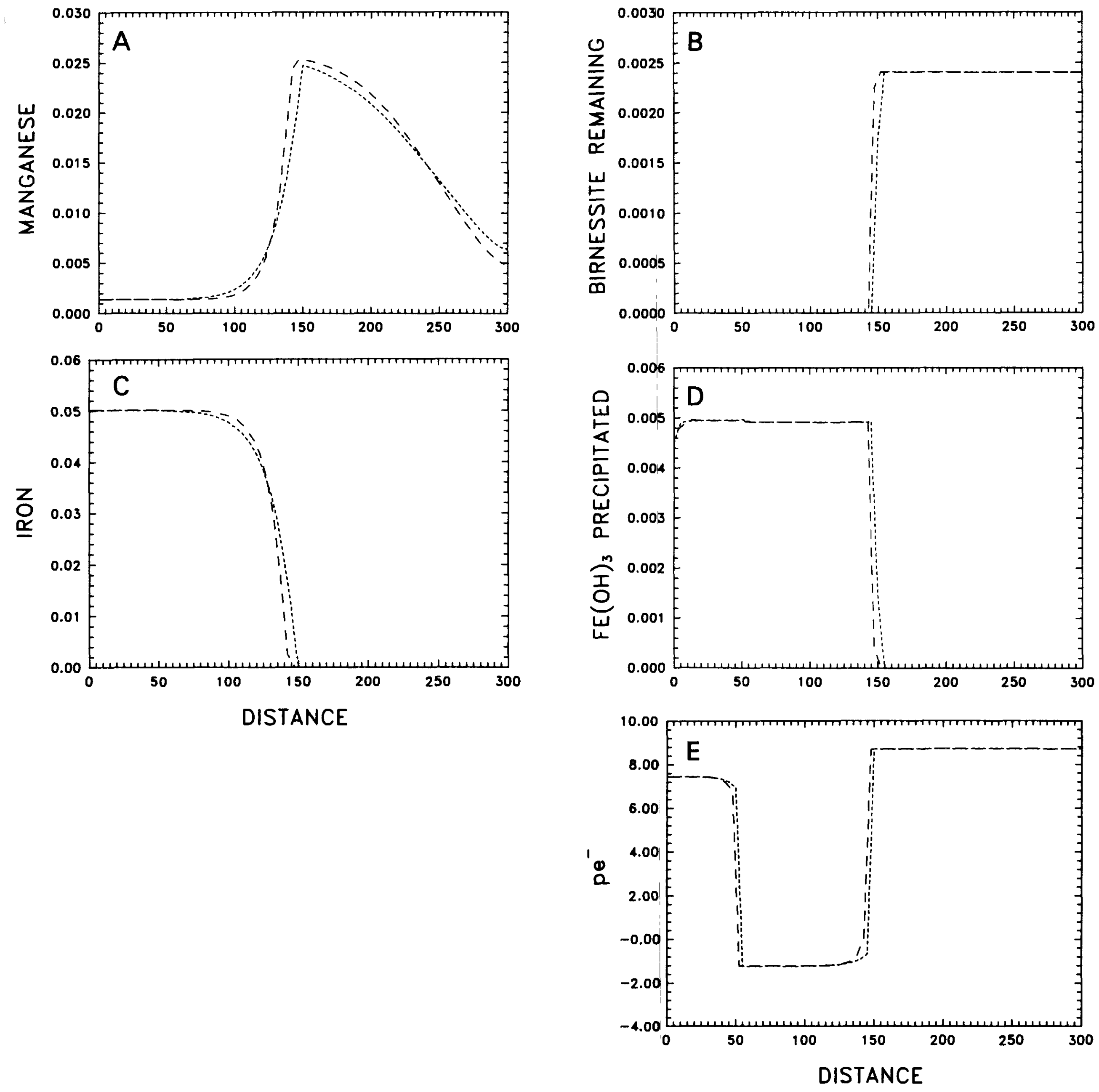

Figure 3. (A-E) Spatial profiles at 50 days of various pe$^-$-dependent total aqueous-concentrations and mineral amounts. The dotted and dashed lines represent the MST1D and PHREEQM results, respectively, in moles per kilogram of H_2O for aqueous concentrations, and in moles per kilogram of solid (bulk density = 2,500 kilograms per cubic meter) for mineral concentrations.

PHREEQM output applies to midcell positions and is, therefore, shifted by 2.5 m with respect to MST1D output.

The geochemical processes simulated can be grouped into two interdependent classes: pH altering processes (figs. 2A-2H) and pe$^-$ altering processes (figs. 3A-3E). After 50 days, pH increases from a value of 4.2 to a value of 7.1 at approximately 50 m. This pH front coincides with the transition from a no-carbonate mineral zone to a dolomite-containing zone. The pH front at 50 m is also reflected by a marked decrease in dissolved aluminum and in H_4SiO_4, by slope-breaks in the SO_4 and Ca curves and by a maximum in the magnesium concentration profile. The pH front also coincides with a sharp decrease in pe$^-$. This pe$^-$ results from a decrease in solubility of $Fe(OH)_3$ at the higher pH, thereby reducing the Fe(III)/Fe(II) ratio and, hence, decreasing pe$^-$.

Another much smaller sudden increase in pH occurs at approximately 150 m, and corresponds to the start of the calcite-containing zone, a maximum Ca concentration, and a drop in dolomite profile back to initial conditions. The increase in pH is best evident in the inorganic-carbon (TDIC) profile. Both PHREEQM and MST1D predict the presence of a sharp dolomite peak at 150 m--a phenomenon that we do not yet fully understand. The initial MST1D run did not show this peak, presumably because of poor resolution.

A sharp increase in pe$^-$ values also occurs at 150 m, corresponding to the end of the $Fe(OH)_3$-containing zone and the start of the birnessite mineral zone. This is reflected in the Fe(II) and Mn(II) profiles. The reduction of birnessite by oxidation of aqueous Fe(II) also causes the release of two protons per mole of birnessite reduced. This process affects the pH of the water and causes calcite to dissolve with an associated precipitation of dolomite because of the high magnesium content of the inflowing solution.

In summary, the reaction of acidic water with pH-neutralizing minerals (calcite, dolomite, microcline, CO_2) leads to three distinct mineralogical zones after 50 days of contaminant transport: (1) a first 50 m zone depleted of all carbonate minerals, that is enriched in secondary gypsum and secondary gibbsite and has experienced some secondary microcline precipitation; (2) a second zone from 50 to 150 m, in which all initial calcite has been dissolved causing the resulting Ca and CO_3 inputs to the solution to combine with the high Mg and SO_4 concentrations of the contaminant water and precipitate dolomite and gypsum (but to a lesser extent than in zone 1); (3) a third zone from 150 m to the end of the column characterized by the the absence of any secondary gypsum and by the presence of calcite, dolomite, and microcline, in amounts virtually unchanged from the initial conditions in the aquifer.

USE AND LIMITATIONS OF PHREEQM AND MST1D

The simulation results given by MST1D and PHREEQM can help conceptualize some of the important geochemical processes affecting the pe^- and pH of ground waters at the Pinal Creek site. Nevertheless, the model results do not bear much resemblance to the situation at Pinal Creek. At the Pinal Creek site, acid-contaminated ground water (with a pH less than 5) has traveled approximately 18 kilometers in 50 years, a similar advance to the 50 m in 50 days simulated in our runs, but that is the extent of any resemblance.

Because of kinetic considerations, dolomite and microcline precipitation should not occur at the Pinal Creek site. Geochemical-transport codes need to have the option of allowing minerals, such as dolomite and microcline, to dissolve but not to precipitate. Ion exchange and adsorption processes are also important processes that need to be incorporated into geochemical-transport codes.

An abrupt pH front is not found at the Pinal Creek site, in contrast to our simulation results. Increasing the value of the effective dispersivity will not affect the sharpness of the pH front in our simulations. In our model, a high pH will result in the presence of carbonate minerals, a low pH will result when all the carbonate minerals have been dissolved away. The dispersivity chosen will only affect the location of the carbonate-mineral zone at a given time. Given the high average ground-water velocity (5 m/d) at the Pinal Creek site, it is reasonable to assume that the local equilibrium assumption is invalid, and that mineral dissolution/precipitation kinetics would have to be taken into account in order to obtain a more realistic simulation (this would be one way to prevent dolomite precipitation). Oxygen diffusion and CO_2 exsolution kinetics in the phreatic Pinal Creek aquifer also need to be taken into account.

Finally, the MST1D and PHREEQM simulations assumed a steady-state one-dimensional flow system, although ground-water flow at Pinal Creek has probably not been in steady-state for the last 50 years; ground-water leakage to/from the underlying Gila Conglomerate and surficial water inputs do occur on a transient basis. A forthcoming two-dimensional version of MST1D may improve the degree of realism in this regard.

SUMMARY

Simulations involving the introduction of acid-contaminated ground water into a carbonate-mineral and birnessite-containing aquifer, using the transport codes PHREEQM and MST1D, give very similar results, providing some confidence in the numerical accuracy of these computer programs. Both codes have their advantages and limitations. PHREEQM currently contains more geochemical options than does MST1D, such as ion exchange and fixed input of reactant components per unit cell per unit time. MST1D, however, probably predicts front positions more accurately, because of its capability to iterate sequentially between the transport and chemical reaction steps. To obtain this accuracy, however, it is essential to use a fine enough time and space discretization to limit the amount of numerical dispersion in the MST1D results. In our example simulation, PHREEQM was not as sensitive to numerical-dispersion problems as MST1D. MST1D has the advantage of being more easily extensible to a two-dimensional code, and has a more flexible set of boundary-condition options (especially those concerning the definition of the flow model). Although, we did not conduct the MST1D and PHREEQM simulations on the same computer, PHREEQM is not as computationally intensive as MST1D, mainly because of PHREEQM's lack of sequential iterations, but also because of PHREEQM's ability to use a larger time step without numerical dispersion problems.

Finally, although PHREEQM and MST1D can be used to help understand the geochemical evolution of contaminated ground waters such as those found at the Pinal Creek toxic waste site, a truly realistic simulation of the site is currently not possible. Nevertheless, MST1D and PHREEQM offer significant improvements over the capabilities of traditional advection-dispersion codes in modeling the evolution of contaminated ground waters dependent on mineral dissolution and precipitation equilibria.

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TRACE-ELEMENT TRENDS AT PINAL CREEK, ARIZONA

By Lynda M. Faires[1] *and* James H. Eychaner[2]

ABSTRACT

Trace-element concentrations vary temporally and spatially in Pinal Creek streamflow. Chemical analysis by inductively coupled plasma-atomic emission spectroscopy during 1979-89 revealed temporal trends of increasing concentrations for dissolved manganese and nickel. Spatial trends were examined by collecting samples from streamflow and shallow ground water at 11 sites in a 6-kilometer perennial-flow reach during March 1990. Spatial trend evaluation for seven trace elements (barium, cadmium, cobalt, copper, molybdenum, nickel, and zinc) was made possible through the use of inductively coupled plasma-mass spectrometry, which provides detection limits one to two orders of magnitude below those of inductively coupled plasma-atomic emission spectroscopy.

INTRODUCTION

The occurrence and movement of acidic contamination in the aquifer and streams of the Pinal Creek basin near Globe, Ariz., where copper has been mined since 1903, is the subject of an ongoing study (Eychaner, 1991a, this Proceedings). The objectives of the study are to identify, describe, and model the processes that control the movement and reactions of inorganic contaminants in surface and ground water in the basin and to monitor the movement of those contaminants. Chemical analysis for major and trace constituents in the basin began in 1979 for surface water and in 1984 for ground water. This paper describes temporal and spatial trends in the trace-element chemistry of streamflow and shallow ground water at Pinal Creek and reports the advantages of using inductively coupled plasma-mass spectrometry (ICP-MS) to determine trace-element concentrations.

HYDROLOGIC SETTING

Streamflow is ephemeral in most of the area, but perennial flow begins in the northern part of Pinal Creek at a location that varies in response to recharge during the previous few years (fig. 1). In August 1985, after above-normal precipitation during 1978-80 and 1982-84, perennial flow began 8.4 km (kilometers) upstream from Inspiration Dam. Beginning in 1987, below-normal precipitation, in combination with aquifer cleanup activities that removed water from the system, caused the head of flow to migrate downstream. Flow began 7.1 km from the dam in January 1988, 6.3 km in March 1990, and 6.1 km in November 1990.

Discharge and water quality have been monitored since 1979 at gaging station 09498400, Pinal Creek at Inspiration Dam (fig. 1). The dam is a cast-concrete structure about 3 m (meters) tall and 24 m long that was built in 1912 at the head of a canyon and abandoned before 1929; it is filled to the crest with sediment. Base flow generally was 0.06 to 0.4 m^3/s (cubic meters per second) during 1980-90. Since 1987, additional water-quality samples have been collected 5.6 km upstream at station 09498380, Pinal Creek at Setka Ranch, where base flow has been about 55 percent of that at Inspiration Dam. In March 1990, about 40 percent of the discharge from the aquifer occurred in the first 0.6 km of streamflow (fig. 2). Water has been diverted 2.4 km upstream from the dam since 1940 and piped 17 km south for use in copper mining.

Ground water that discharged to Pinal Creek in March 1990 contained 2,800 to 3,700 mg/L (milligrams per liter) of dissolved solids, principally Ca (calcium) and SO_4 (sulfate), and had a pH of 5.8 to 6.8 and temperature of 14° to 19 °C (degrees Celsius). Dissolved-oxygen concentration was less than 1 mg/L. Upgradient in the aquifer south of well site 400 (Eychaner, 1991a, this Proceedings, fig. 1), however, water in a contaminant plume had a pH of less than 4 and contained more than 5,000 mg/L SO_4; 1,000 mg/L Fe (iron); 100 mg/L Al (aluminum) and Cu (copper); 2 mg/L Co (cobalt), Ni (nickel) and Zn (zinc); and 0.2 mg/L Ba (barium) and Cd (cadmium).

Reactions between aquifer material and acidic water raise the pH and retard the movement of many contaminants relative to the movement of the water itself. Each contaminant moves at a different rate as a result of the interaction of its pH-dependent solubility, oxidation state, and ease of sorption on solid surfaces. Although some contaminants have already appeared in Pinal Creek streamflow, large concentrations of other contaminants are not expected to reach the creek for several years.

ANALYTICAL METHODS

Quantitative measurement of concentrations of dissolved inorganic consituents in water samples is commonly determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) or ICP-MS. Both techniques are capable of rapid multielement analysis for most metals (Faires, 1986; Faires, in press). Detection limits for ICP-AES are in the range of 3 to 20 µg/L (micrograms per liter) for most elements, but ICP-MS is able to achieve routine detection limits in the range of 0.3 to 1.0 µg/L for most elements.

Since 1979, most of the chemical analyses for dissolved-element concentrations were conducted using ICP-AES by K.G. Stollenwerk (U.S. Geological Survey, Lakewood Colo.) ICP-MS was used by L.M. Faires, for samples collected in March 1990. Water temperature, specific conductance, pH, dissolved-oxygen concentration, platinum-electrode potential, and alkalinity were measured in the field at the time of sampling. Anion concentrations were measured in laboratory.

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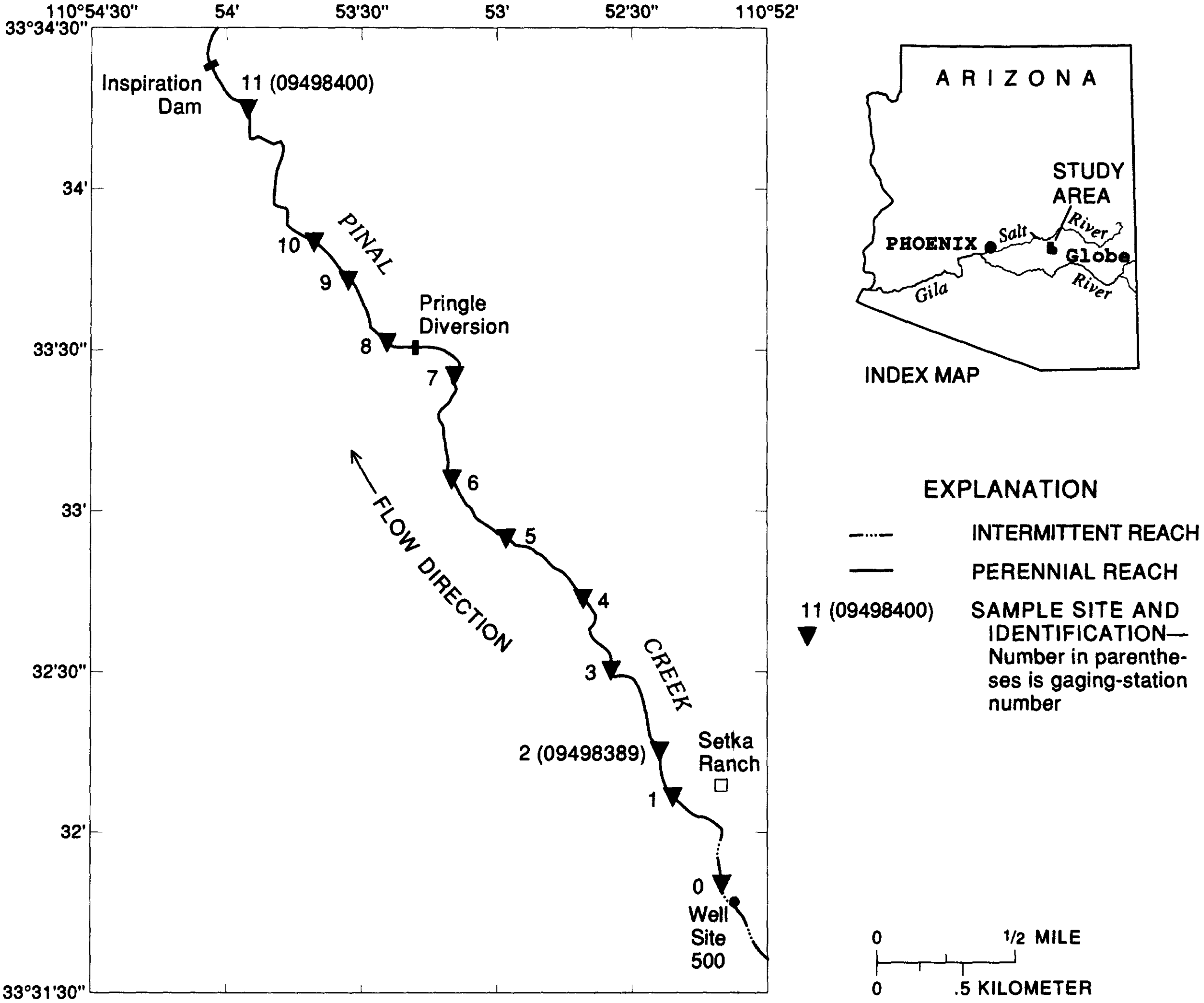
110°54'30"
54'
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Inspiration Dam
11 (09498400)
10
9
8
7
6
5
4
3
2 (09498389)
1
0
Pringle Diversion
Setka Ranch
Well Site 500
PINAL
CREEK
FLOW DIRECTION
ARIZONA
STUDY AREA
PHOENIX
Salt River
Globe
Gila River
INDEX MAP
EXPLANATION
INTERMITTENT REACH
PERENNIAL REACH
11 (09498400)
SAMPLE SITE AND IDENTIFICATION—Number in parentheses is gaging-station number
0
1/2 MILE
0
.5 KILOMETER

Figure 1. Area of study and sites sampled March 6-8, 1990.

TIME TRENDS

Data for 1979-89 were used to interpret the geochemistry of the area and to determine temporal trends in constituent concentrations in streamflow. Dissolved-solids concentration in streamflow at Inspiration Dam increased from about 2,700 mg/L in 1979 to about 3,500 mg/L in 1989, despite temporary decreases during 1983-85 (fig. 3). Dissolved SO_4 concentration increased to about 2,100 mg/L in 1989. About a third of the inorganic carbon in the ground water degasses from Pinal Creek as the water equilibrates with the atmosphere; resulting changes in dissolved carbonate species increase the pH by about 2 units at the dam compared to the ground water. Dissolved-oxygen concentration increases concurrently.

The concentration of dissolved Mn (manganese) at Inspiration Dam increased from 0.5 mg/L in 1979 to about 35 mg/L during 1988-89 (fig. 3). Upstream at Setka Ranch, the concentration of dissolved Mn averaged 72 mg/L during 1989, but Mn concentration decreases downstream as pH and dissolved-oxygen concentration increase, and black Mn oxides precipitate on the streambed (Eychaner, 1991b, this Proceedings). Streambed sediments, however, provide only a temporary sink for Mn because flood discharges break up and transport the weakly cemented sediments.

At Setka Ranch, the concentration of dissolved Ni began to increase in 1988, followed by a decrease in alkalinity and an increase in concentration of dissolved Fe in 1989 (fig. 4). At Inspiration Dam, however, no measurable changes in concentrations of these constituents had occurred by July 1990.

SPATIAL TRENDS

In March 1990, streamflow samples were collected at 11 sites in the perennial reach of Pinal Creek (fig. 1) to compare the analytical methods of ICP-AES and ICP-MS for trace-element determinations; to estimate the spatial distribution of the rate and solute concentration of ground-water discharge; and to evaluate the interactions among pH, Mn precipitation, and gas exchange with the atmosphere. Ground-water samples were collected at about 1.5 m below the water table at the 11 sites and at a 12th site upgradient from the beginning of surface flow.

These water samples were analyzed by ICP-AES and ICP-MS. The high specific conductance of the samples required dilution by a factor of 10 before analysis by either

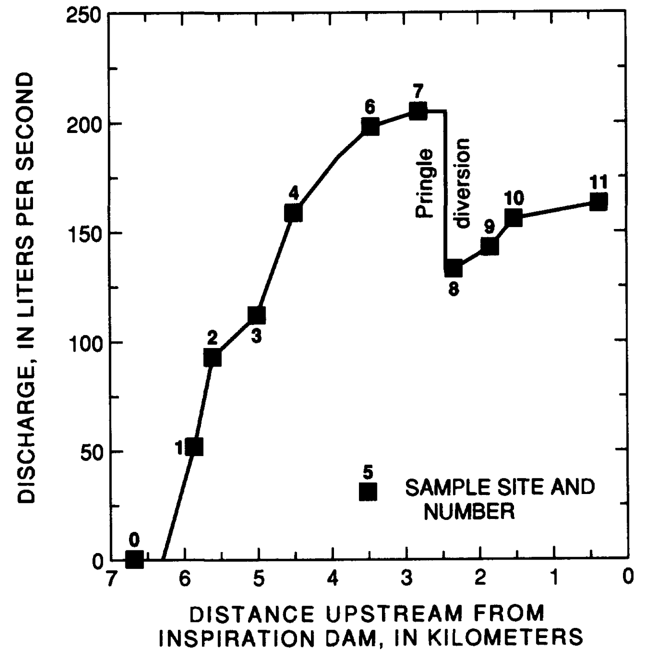

Figure 2. Discharge in the perennial reach of Pinal Creek, March 5-9, 1990.

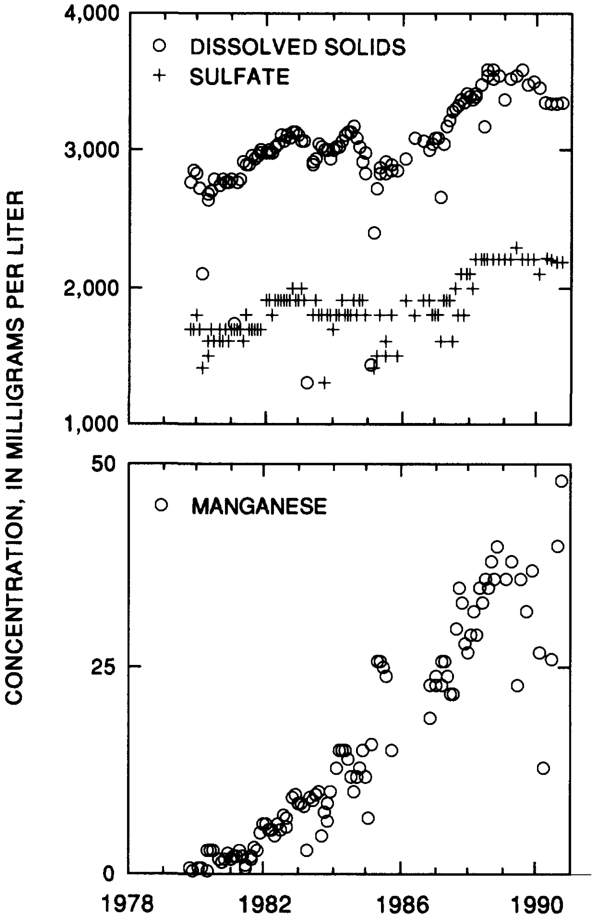

Figure 3. Dissolved-solids, sulfate, and manganese concentrations in streamflow at station 09498400, Pinal Creek at Inspiration Dam, 1979-90.

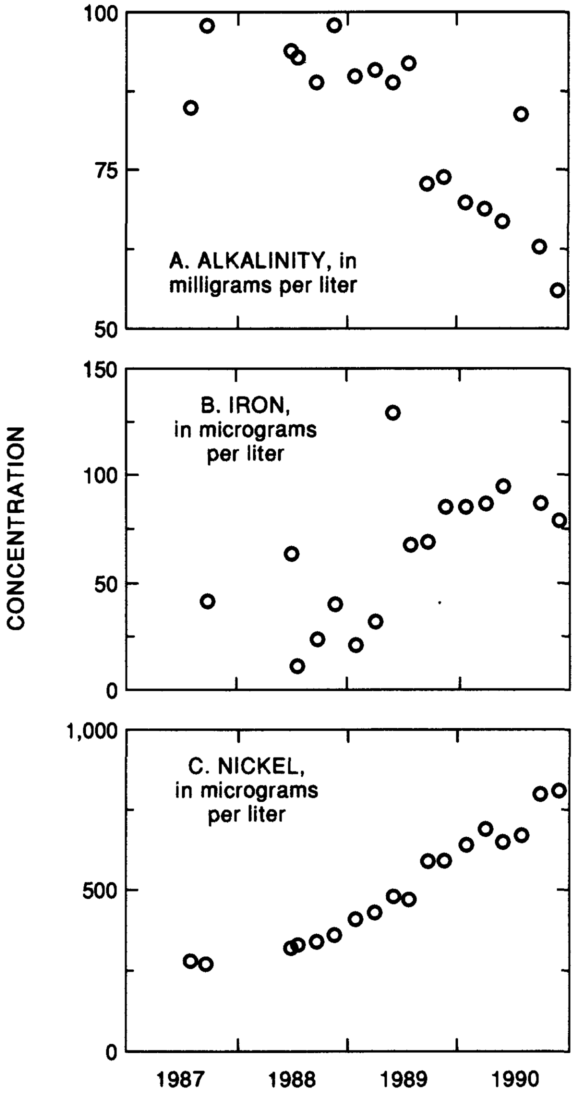

Figure 4. Alkalinity, dissolved-iron, and dissolved-nickel concentrations in streamflow at station 09498380, Pinal Creek at Setka Ranch, 1987-90.

technique to prevent physical and spectral interferences. Sample dilution results in a corresponding increase in the analytical detection limits in the sample. Using ICP-AES, the concentrations of Ca, Mg, Na, Si, Mn, Sr, and Ni were determined. Elevated concentrations of Mn and Ni were detected in some samples, but the concentrations of most trace elements in these diluted samples were below the detection limits of the ICP-AES technique. Even after dilution, the ICP-MS technique was capable of quantitation of many trace elements (Mn, Ni, Zn, Ba, Co, Cu, Cd, Mo) so that the spatial changes in concentrations of these elements could be monitored in both the surface- and ground-water samples.

Concentrations of the elements determined by ICP-AES generally were 2 to 650 mg/L and varied along the sampling sites (fig. 5). With the exception of Mn, the concentrations of each element were similar in the surface and ground water at each site and remained approximately constant along the extent of the sampled area. Mn concentration in ground water decreased to below ICP-AES detection limits by site 6 but decreased more gradually in the streamflow because of mixing and transport.

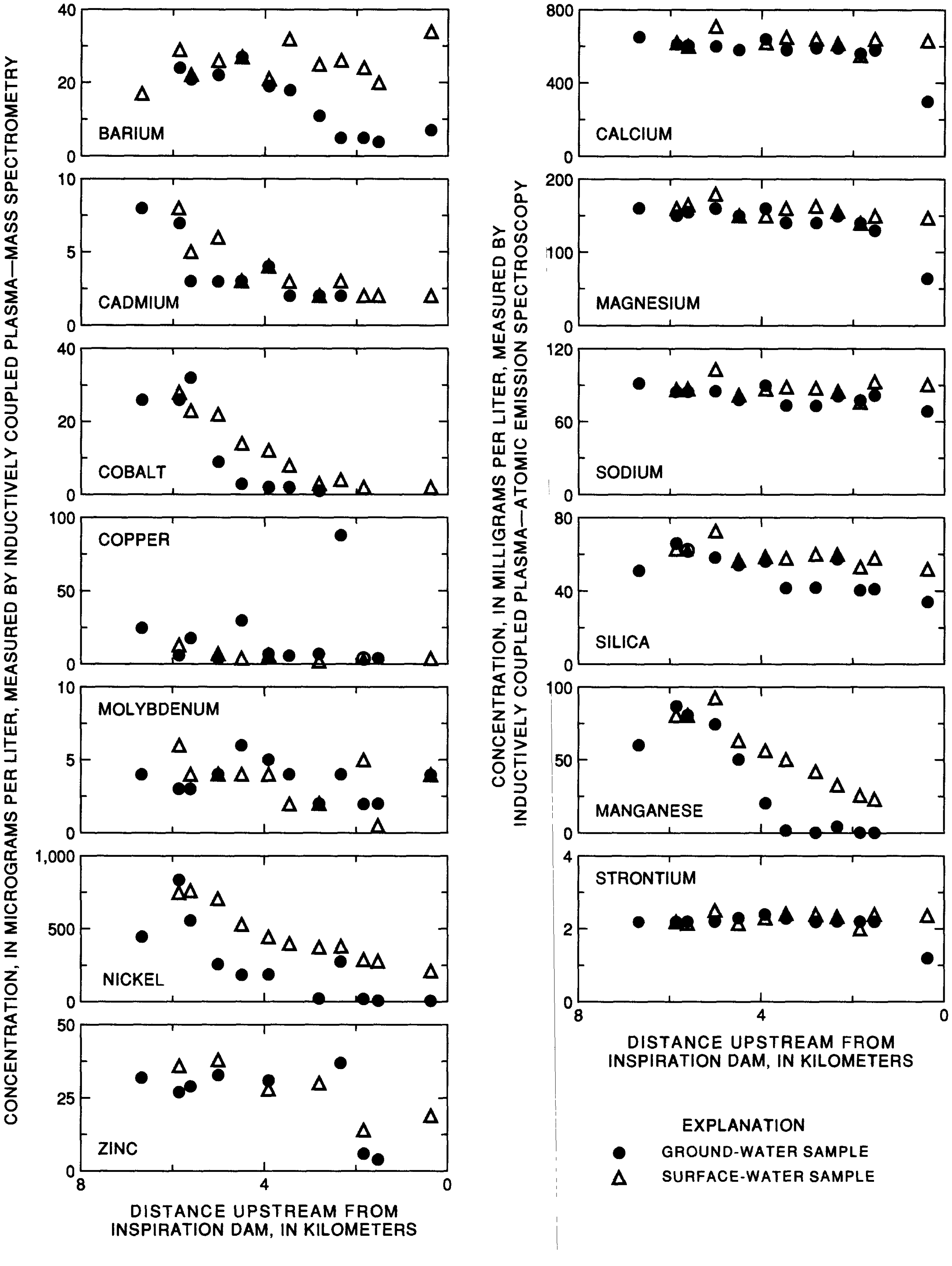

Figure 5. Concentration of dissolved constituents in water samples, March 1990.

Concentrations of the elements determined by ICP-MS generally were less than 40 ug/L and varied significantly along the sampling sites (fig. 5). The spatial trends in concentrations for each trace element were distinctly different in surface water compared to ground water, although the concentrations at the most upstream site were similar. In the surface water, the concentrations of all the trace elements decreased, with slight fluctuations, along the sampling area, from site 1 to site 11.

In the ground water, each trace element exhibited a unique spatial trend. Concentrations of Ba and Mo remained approximately constant from site 1 to site 11. The concentration of Ni gradually decreased from site 1 to site 11 except for an increase at site 8. At sites 4 and 8, concentrations of Zn increased significantly and those of Mo increased slightly. Cu concentration increased signficantly at sites 2, 4, and 8. Concentrations of Co and Cd had a different pattern; Co concentration decreased downstream of site 2, and Cd concentration decreased to a low and virtually constant level downstream of site 1. Given the small concentrations of the trace elements, sorption on manganese oxides is the most likely process controlling their concentrations. Stollenwerk (1990) showed that sorption on hydrous ferric oxides is sufficient to explain the distribution of Co, Cu, Ni, and Zn in ground water between well sites 100 and 500 (Eychaner, 1991a, this Proceedings, fig. 1).

Specific conductance and anion concentrations were similar in the surface- and ground-water samples and remained virtually constant from site 1 to site 11, except that SO_4 concentration increased in the ground water at site 8, where Ni, Zn, and Cu concentrations also increased. The pH of the ground water was about 5.9 at sites 0 through 4 and increased to about 6.7 at sites 6 through 11, except for site 8, where pH was 5.8. Streamflow pH generally was higher than ground water pH and increased downstream from about 6.0 to about 7.5.

CONCLUSIONS

Chemical analysis of the physical properties and concentrations of dissolved elements in samples of streamflow and ground water provides essential information for monitoring the occurrence and movement of acidic contamination in the Pinal Creek basin. The lower detection limits attainable by inductively coupled plasma-mass spectrometry (ICP-MS), compared to inductively coupled plasma-atomic emission spectroscopy (ICP-AES), provides additional information on the concentration and distribution of trace elements. The spatial trends of concentration of these trace elements are different in the streamflow compared to the ground water, and the information provided by ICP-MS analysis will enhance the monitoring and understanding of the movement of inorganic contaminants in this study area.

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EFFECT OF IMPURITIES IN GYPSUM ON CONTAMINANT TRANSPORT AT PINAL CREEK, ARIZONA

By Pierre D. Glynn[1]

ABSTRACT

Secondary gypsum is present in alluvial sediments at the Pinal Creek acidic mine drainage site near Globe, Arizona. The gypsum forms from reaction of the acidic ground-water plume with detrital carbonate minerals, and contains impurities that reflect the composition of the contaminated water. Distribution coefficients measured for strontium, sodium, and magnesium agree with previously published results for gypsum coprecipitation from brines. Measured impurity mole-fractions are very small (strontium, 0.051 percent; sodium, 0.044 percent; aluminum, 0.04 percent; iron, 0.026 percent; potassium, 0.0075 percent; vanadium, 0.00701 percent; magnesium, 0.004 percent; manganese, 0.002 percent; molybdenum, 0.002 percent; barium, 0.0014 percent; chromium, approximately 0.0009 percent; cobalt, approximately 0.0008 percent; nickel, approximately 0.002 percent; copper, less than 0.001 percent; cadmium, 0.00018 percent; lead, approximately 0.00016 percent). Theoretical considerations suggest that these impurities do not significantly change the solubility product of gypsum. Nevertheless, the molybdenum, vanadium, barium, strontium, and cadmium impurities are high enough, relative to the contaminated water concentrations, that they may have to be considered in modeling reactions and transport of these elements at the Pinal Creek site. Results of analyses of strontium in carbonate rocks from formations surrounding the Pinal Creek Valley, together with results of analyses of strontium in gypsum precipitated in the aquifer, suggest that the strontium increase that accompanies the neutralization of acid-contaminated ground water does not come solely from the dissolution of carbonate minerals. Feldspar dissolution is suggested as a significant source of strontium to the acidic ground water. A budget of the redox-independent reactions capable of consuming or releasing protons to the water is constructed using the strontium mass balance.

INTRODUCTION

Contaminated ground water sampled from the Pinal Creek Toxic Waste site is commonly slightly supersaturated with respect to gypsum. Gypsum saturation indices range from 0.02 to 0.09. Many filtered ground-water samples, from wells 452, 501, 503 and 505, for example, (fig. 1) were found to precipitate gypsum after being brought back to the laboratory, even though the increase in temperature relative to that of the ground-water environment should cause an increased gypsum solubility. Gypsum precipitation and, possibly, jarosite, alunite, and $AlOHSO_4$ precipitation in the most acidic ground waters, are the only mineral controls on the amount of sulfate present in Pinal Creek ground waters. Although sulfate is, in itself, a relatively innocuous contaminant, sulfate does form very strong complexes with several of the contaminant metals of concern, such as copper, zinc, nickel, cadmium, iron, manganese, and aluminum. Gypsum precipitation is, therefore, important in limiting the flux of dissolved metals in Pinal Creek ground water. Percentages of metals complexed by sulfate are given in table 1 for three ground waters sampled from the Pinal Creek site in August 1987. The percentages were determined using the speciation model WATEQ4F (Ball and others, 1987). Metal-sulfate complexes typically comprise more than 30 percent of total dissolved metals and are by far the most predominant complexes, the only exception being the aluminum fluorides.

The first objective of this study was to determine the amounts of impurities present in gypsum from the Pinal Creek toxic waste site, and to assess whether gypsum supersaturation observed in Pinal Creek ground waters could be caused by solid-solution impurities that increase the solubility of the mineral. A second objective was to determine whether gypsum solid-solutions could constitute an important reservoir of contaminant ions--one that would need to be considered in modeling the reaction and transport of dissolved metals in Pinal Creek ground waters. Finally, a third objective was to determine the importance of carbonate-mineral dissolution, relative to silicate-mineral dissolution, in neutralizing acidic ground waters at the Pinal Creek site. An attempt was made to achieve this objective by comparing the amounts of strontium and barium taken up during gypsum precipitation to the amounts of those elements released during carbonate-mineral dissolution. This paper presents the results of that study.

ACKNOWLEDGMENTS

I am grateful to Ed Busenberg for his analyses of major cations in gypsum and to Ray van Hoven for his analysis of gypsum from well 503 and in particular for his determination of selenium by the hydride generation technique. I also extend my appreciation to Stephanie Dunkle for her carbonate-rock analyses.

EXPERIMENTAL RESULTS

Three gypsum samples were analyzed from the Pinal Creek site. Eychaner (1989) provides a thorough description of the Pinal Creek Toxic Waste site and of the various wells and localities mentioned in this paper. The first sample (A1) consisted of 1-cm (centimeter) long selenite crystals and was obtained by K.G. Stollenwerk of the U.S. Geological Survey from the drill cuttings of well 51. Well 51 has the most acidic ground water found at the Pinal Creek site. A second gypsum sample (A2) was obtained by the author in September 1988 from the drained bed of Webster Lake. Until it was drained in 1988, Webster Lake was used to receive waste sulfuric acid from copper-refining industries and it had a pH of about 2.7.

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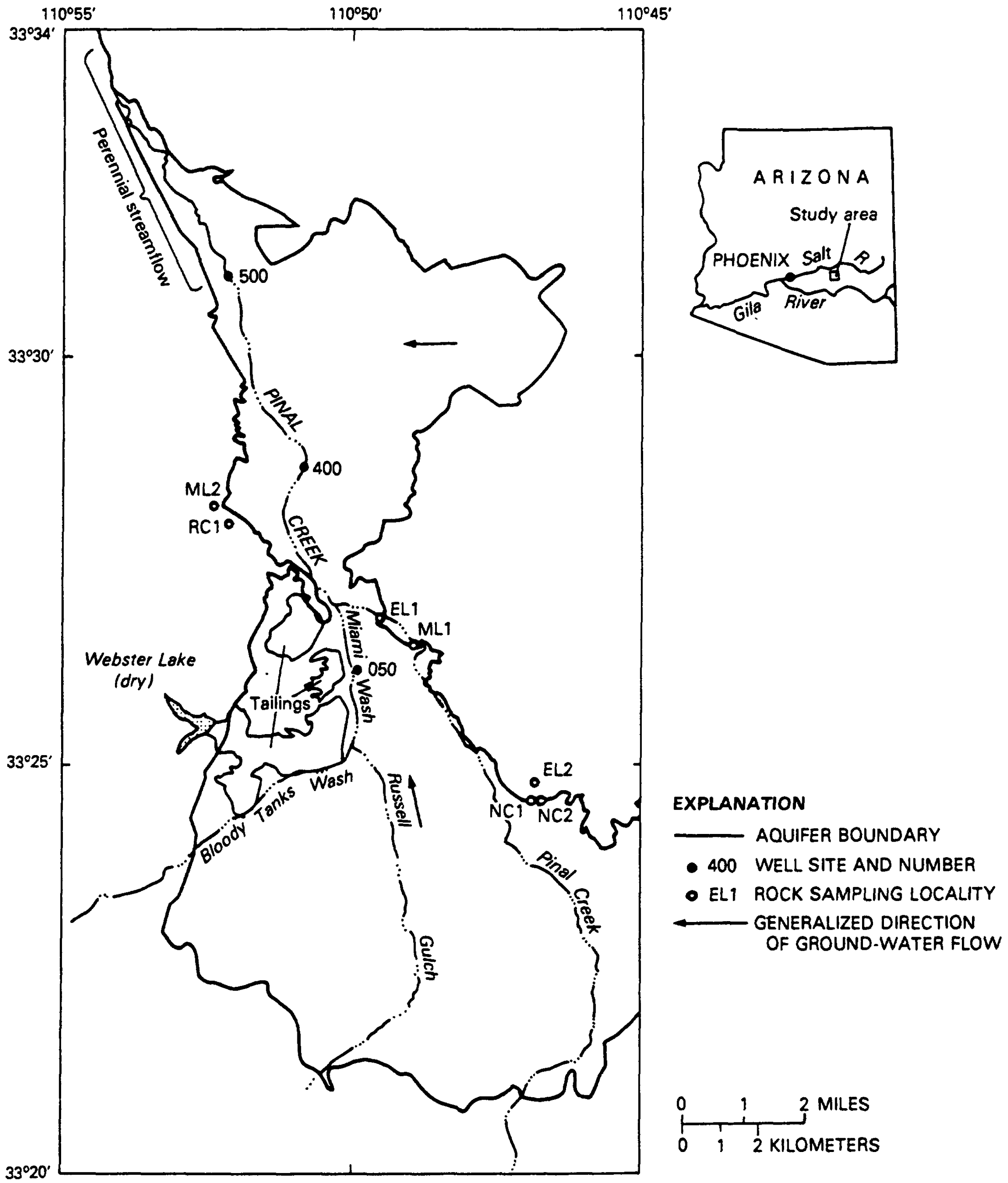
110°55'
110°50'
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33°34'
33°30'
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33°20'
Perennial streamflow
500
PINAL
400
CREEK
ML2
RC1
EL1
ML1
050
Miami Wash
Webster Lake (dry)
Tailings
Bloody Tanks Wash
Russell Gulch
EL2
NC1
NC2
Pinal Creek
ARIZONA
Study area
PHOENIX
Salt R.
Gila River
EXPLANATION
AQUIFER BOUNDARY
● 400 WELL SITE AND NUMBER
○ EL1 ROCK SAMPLING LOCALITY
GENERALIZED DIRECTION OF GROUND-WATER FLOW
0 1 2 MILES
0 1 2 KILOMETERS

Figure 1. The Pinal Creek site: area of study and sample collection sites. NC1, NC2, EL1, EL2, ML1, ML2, and RC1 are rock sampling locations. Wells 404 and 402 mentioned in the paper are located at well site 400. Well 51 is located at site 050, wells 503, 505, and 501 at site 500.

Table 1. *Percentages of total dissolved metals complexed by sulfate*

[Sulfate (SO_4), in moles per liter]

			Mole percent of metal complexed by sulfate						
Well	pH	SO_4	Fe	Mn	Al	Cu	Zn	Cd	Ni
51	3.74	2.9	38.7	38.3	[1]72.1	43.9	55.6	57.4	42.4
402	4.27	34.5	33.7	33.4	0.73	38.5	41.1	[3]NA	59.8
503	6.07	20.9	[2]ND	26.7	[2]ND	[2]ND	[2]ND	ND	25.7

[1] No fluoride data available for this analysis.

[2] Element not detected.

[3] No analysis.

Table 2. *Mole fractions of analyzed impurities (direct coupled plasma analyses)*

		Constituent, in mole percent							
Sample	Origin	Ca	Sr	Fe	Mn	Na	K	Mg	Ba
A1	Well 51 core	99.795	0.051	0.026	0.002	0.044	0.0076	0.005	0.0014
A2	Webster lake	99.669	.024	.13	.0041	.055	.027	.032	.00023
A28	Well 503 water	99.886	.036	.026	.0026	.036	.0089	.0037	.00013

Table 3. *Mole fractions of analyzed impurities (graphite furnace analyses)*

[<, less than]

	Constituent, in mole percent									
Sample	Mo	Co	Ni	Cu	Cd	Cr	Se	Al	Pb	V
A1	0.0019	0.00082	0.0016	<0.001	0.00018	0.00087	[1]0.014	0.040	<0.0002	0.0070
A2	.0022	.00072	.0014	.003	.00014	.0014	[1].0095	.033	<.0002	.0041
A28	[2]<.06	<.001	<.0006	<.0003	<.0002	[3]NA	[4]<.0002	.051	<.0003	[2]NA

[1] Analysis needs to be repeated by hydride-generation atomic-absorption spectrosopy.

[2] Direct coupled plasma analysis.

[3] No analysis.

[4] Hydride generation technique.

Today, the lakebed is covered by deposits rich in gypsum and jarosite. Large selenite clusters with blades up to 10-cm-long (from which sample A2 was collected) are found on dead wood deposited on the lakebed. In contrast to samples A1 and A2, the third gypsum sample (A28) was not formed in an acidic water. Sample A28 was obtained from a 2.5-liter sample of filtered unacidified water collected in June 1988 from well 503. After 4 months of storage in a tightly sealed glass bottle held at room temperature (approximately 22 °C (degrees Celsius)), 1.20 g (gram) of solid were found to have precipitated. X-ray analysis confirmed that the solid precipitated was gypsum.

Samples A1 and A2 were cleaved into inclusion-free pieces (as far as could be seen using a 3x binocular microscope), and surficially cleaned by partial dissolution in distilled deionized water. Sample A28 was filtered from its mother liquor, washed with 100-percent methanol and air-dried at room temperature. The three gypsum samples were then dissolved in hydrochloric acid.

The gypsum samples were analyzed for sodium (Na), magnesium (Mg), calcium (Ca), potassium (K), strontium (Sr), barium (Ba), iron (Fe), manganese (Mn) by direct-coupled plasma (DCP) spectrophotometry. Graphite-furnace (GF) atomic-absorption spectrophotometry was used to analyze for copper (Cu), nickel (Ni), zinc (Zn), cadmium (Cd), chromium (Cr), lead (Pb), aluminum (Al), vanadium (V) and molybdenum (Mo). Results of the gypsum analyses are given as mole fractions of total cations in tables 2 and 3.

Carbonate-rock samples from the Martin, Escabrosa, and Naco Limestones of Paleozoic age and calcite coatings from a Tertiary rhyolite deposit were collected, by the author in December 1988, from the hills bordering the Pinal Creek Valley (see Petersen, 1962, for a geological description of the rock units flanking the Pinal Creek Valley). Locations of sample collections are given in figure 1. The samples were dissolved in nitric acid (after initial surficial acid cleaning) and analyzed for Sr, Ba, Mg, Ca, Na, and K by DCP spectrophotometry. Results are given in table 4.

GYPSUM SOLID-SOLUTION THERMODYNAMICS

The water sample from well 503 had to have a gypsum saturation index of at least 0.09 in order to precipitate 1.20 g of gypsum at room temperature, (PHREEQE) (Parkhurst and others, 1980). Our objective was to determine if such a degree of supersaturation could be the result of solid-solution impurities in the gypsum.

Table 4. *Mole-fractions of total analyzed cations in carbonate rocks*

		Constituent, in mole percent							
Sample	Origin	Ca	Mg	Sr	Ba	Fe	Mn	Na	K
RC1	Rhyolite (joint filling)	98.75	0.93	0.013	0.00091	0.0516	0.0068	0.091	0.159
EL1	Escabrosa Ls	97.16	2.66	.0023	.00148	.0971	.0613	.01	.0063
EL2	Escabrosa Ls	99.22	.69	.0059	.0002	.0412	.0081	.01	.0304
ML1	Martin Ls	53.67	45.34	.0074	.0006	.8417	.0620	.05	.0379
ML2	MartinLs	98.88	1.09	.0094	.0002	.002	.0002	.01	.0064
NL1	Naco Ls	98.28	1.51	.0263	.0004	.127	.0347	.02	.002
NL2	Naco Ls	97.38	2.36	.0350	.0004	.163	.0231	.03	.0059

The maximum solubility of a solid-solution is achieved when the solid behaves as a one-component solid of fixed composition. The equilibrium state reached between a solid-solution and an aqueous solution given this constraint is called "stoichiometric saturation" (Thorstenson andPlummer, 1977; Glynn, 1990; Glynn and Reardon, 1990; Glynn and others, 1990; Glynn, and others, in press). Unless it happens to coincide with true (multicomponent) thermodynamic equilibrium, stoichiometric saturation must be considered a metastable saturation state.

Assuming that the gypsum solid-solutions formed at the Pinal Creek site could dissolve congruently to a state of stoichiometric saturation, the gypsum saturation index SI_{gyp} observed could be expressed by the equation (Glynn, 1990):

$$SI_{gyp} = -\log K_{gyp} + \log \left[K_{ss} \left(\frac{\chi_{gyp,aq}}{\chi_{imp,aq}}\right)^{x} \right], \qquad (1)$$

where

$$K_{ss} = K_{gyp}^{1-x} K_{imp}^{x} x^{x} (1-x)^{1-x} \exp\left[a_o x (1-x)\right]. \qquad (2)$$

K_{ss} is the stoichiometric saturation constant. K_{gyp} is the solubility product of "pure" gypsum ($10^{-4.58}$ according to Langmuir and Melchior, 1985). The gypsum saturation index SI_{gyp} is defined as the logarithm of the ratio of the calcium-sulfate ion-activity product divided by K_{gyp}. K_{imp} is the solubility product of an imaginary "impurity endmember" and x is the mole-fraction of this "impurity endmember"; a_0 is the dimensionless excess-free-energy-of-mixing parameter (Guggenheim, 1937; King, 1969). $\chi_{gyp,aq}$ and $\chi_{imp,aq}$ are the aqueous "activity-fractions" of the gypsum and impurity endmembers in the aqueous-solution (see Glynn and Reardon, 1990, for further explanation of these parameters).

An expression describing SI_{gyp} in the case of dissolution of gypsum into initially pure water, or a more general case for which $\chi_{gyp,aq}/\chi_{imp,aq} = (1-x)/x$, can be derived from equation 1. The stoichiometric saturation state described is called a "minimum stoichiometric saturation" state by Glynn and Reardon (1990):

$$SI_{gyp} = x \log \left(\frac{K_{imp}}{K_{gyp}}\right) + \log(1-x) + \frac{a_o x(1-x)}{\ln(10)} \qquad (3)$$

The assumptions used in formulating the above equations are: (1) the impurities measured are solid-solution impurities that substitute only for the Ca ion and that can be grouped into a single thermodynamic component, and (2) a regular solid-solution model (with a single excess-free-energy parameter a_0) is applicable. With these assumptions, equation 3 can be used to calculate the gypsum saturation index of a solution at stoichiometric saturation for a range of possible a_0 and K_{imp} values.

Figure 2 represents an array of possible log K_{imp} and a_0 values well beyond what might be expected for gypsum precipitated from Pinal Creek ground water. In fact, if an impurity mole-fraction of 0.2 percent (that is the average impurity mole-fraction determined in Pinal Creek gypsum) were to represent the highest amount of impurities that could be incorporated into gypsum without making the mineral thermodynamically unstable--that is, if 0.2 percent were to correspond to the miscibility gap limit--the maximum a_0 value that could be expected would be 6.23 (according to MBSSAS, a computer code for the computation of Margules

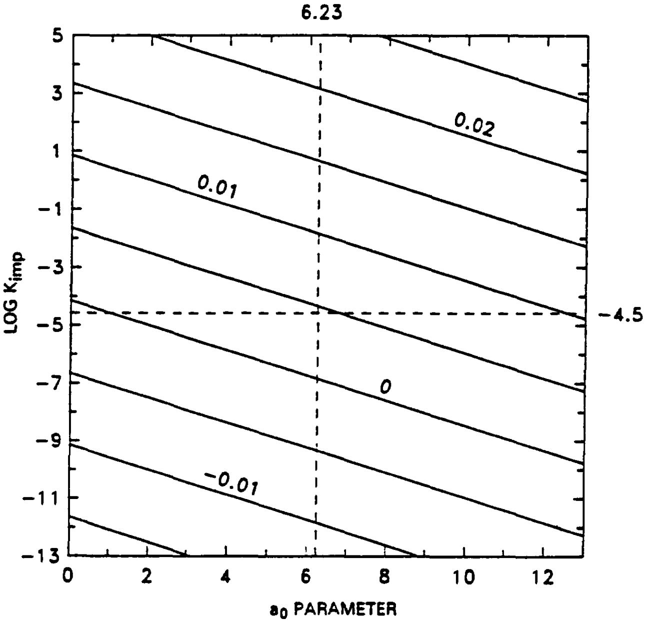

Figure 2. Gypsum saturation indices as a function of the solubility product (K_{imp}) of an "impurity endmember" and of the excess-free-energy-of-mixing parameter a_0. The dashed lines refer to the conditions a_0 = 6.23 and log K_{imp} = -4.58.

parameters and equilibrium relations in Binary Solid-Solution Aqueous-Solution systems (Glynn, in press).

Sodium is the second most abundant impurity in gypsum (after strontium) and it is also one of the most soluble impurities in gypsum--that is, it is one of the most leachable to an aqueous phase. The logarithm of the solubility product of mirabilite, $Na_2SO_4 \cdot 10H_2O$, is -1.21 (Plummer and others, 1988)--a value well below the maximum log K of +5 given in figure 2 but above the log K of pure gypsum (-4.58 according to Langmuir and Melchior, 1985).In comparison, the logarithm of the solubility product of celestite, $SrSO_4$, the dominant impurity in the gypsum samples, is -6.63 (Reardon and Armstrong, 1987) well below that of pure gypsum. As a result, strontium would tend to lower the SI_{gyp} at stoichiometric saturation, whereas sodium would tend to increase it. In any case, the greatest SI_{gyp} value that could be explained using solid-solution thermodynamic theory would be in the 0.02 to 0.03 range for a 99.8-percent pure gypsum solid-solution. Analysis errors could well be of such magnitude.

Figure 2 (and equation 3) reveal an interesting feature of solid-solution thermodynamics. If the solubility product of the "impurity endmember", K_{imp}, is equal to that of the gypsum endmember ($K_{gyp} = 10^{-4.58}$), and if the solid-solution formed is ideal (a_0=0), the computed SI_{gyp} value will be slightly smaller than 0. This feature is caused by the configurational entropy of mixing, which always has a positive value for $0 < x < 1$. This effect can be canceled (such that SI_{gyp}=0) by a repulsive energy-of-mixing. For an impurity mole-fraction of 0.2 percent, an a_0 value of 1.003 is needed. For smaller impurity fractions, a_0 would asymptotically approach a value of 1. For the maximum impurity fraction of 0.5 (50 percent), an a_0 value of 2.77 would be needed to obtain an SI_{gyp} value of 0. These results have implications regarding the difference in solubility between isotopically pure minerals and common minerals. For example, consider that the average abundance of sulfur 34 (^{34}S) in gypsum is approximately 4.2 percent (Pearson and Rightmire, 1980), and assume that sulfur 32 (^{32}S) is the only other isotope present in gypsum. Also assume that the remaining elements in gypsum, Ca, oxygen (O) and hydrogen (H), are all isotopically pure. The observed equilibrium enrichment of ^{34}S between gypsum and aqueous sulfate is 1.65 per mil (Thode and Monster, 1965; discussed in Pierre, 1989). This enrichment factor corresponds to an isotope fractionation factor of 1.00165, and the fractionation factor is numerically equivalent to the ratio of the solubility products of pure $Ca^{34}SO_4 \cdot 2H_2O$ and pure $Ca^{32}SO_4 \cdot 2H_2O$ if an ideal "isotopic solid-solution" is assumed. With this assumption (a_0=0), equation 3 yields the result, SI_{gyp34} = 0.042 log(0.99835) + log(0.958) = -0.00003 - 0.01863 = - 0.01866. Therefore, a solution at stoichiometric saturation with naturally occurring $CaSO_4 \cdot 2H_2O$ should be undersaturated with respect to isotopically pure $Ca^{32}SO_4.2H_2O$ by an SI value of about -0.02!

Figure 2 shows that the supersaturation of well 503 with respect to gypsum ($SI_{gyp} \geq 0.09$) cannot be explained by solid-solution thermodynamics. It may be argued instead that Pinal Creek ground waters are commonly slightly supersaturated with respect to gypsum, because a certain degree of supersaturation must be achieved before precipitation rates can become high enough to balance the input of calcium ions from the dissolution of carbonate and silicate minerals. Impurities in the precipitating gypsum and in the ground water could well have a surface-poisoning effect on the kinetics of gypsum precipitation, but this remains to be demonstrated.

THE GYPSUM-IMPURITY RESERVOIR

The incorporation of impurities into a mineral phase not only affects the thermodynamic stability of the solid phase as discussed in the previous section but may also control the concentration of impurities (or contaminants) in a contacting aqueous phase. Solid-solution formation causes retardation in the transport of a contaminant through an aquifer and may also be responsible for the later release of the contaminant into a "cleaned-up" ground water. The partitioning of an impurity between solid and aqueous phases can be controlled by thermodynamic and kinetic factors. This partitioning is usually expressed in terms of a distribution coefficient D. Using the example of strontium substitution for calcium in gypsum, the practical "experimental" definition of D is:

$$D = \frac{\chi_{Sr}}{\chi_{Ca}} / \frac{m^T_{Sr}}{m^T_{Ca}}, \tag{4}$$

where χ_{Sr} and χ_{Ca} are the mole fractions of strontium and calcium in gypsum, $m^T{}_{Sr}$ and $m^T{}_{Ca}$ are total molalities of strontium and calcium in the aqueous solution. The above definition of distribution coefficients is independent of any aqueous-model calculations.

If the distribution coefficient measured represents an equilibrium distribution of strontium and calcium between gypsum and an aqueous-solution, then the following relation should hold:

$$D = \frac{K_{gyp}}{K_{cel}} \frac{\gamma_{gyp}}{\gamma_{cel}} \frac{f_{Sr}{}^{2+} \gamma_{Sr}{}^{2+}}{f_{Ca}{}^{2+} \gamma_{Ca}{}^{2+} [H_2O]^2}, \tag{5}$$

where K_{gyp} and K_{cel} represent the solubility products of the pure gypsum and celestite endmembers; γ_{gyp} and γ_{cel} are the activity coefficients of the gypsum and celestite components in the solid-solution; $f_{Ca}2+$ and $f_{Sr}2+$ are the "speciation" fractions of aqueous Ca^{2+} and Sr^{2+} ions to total aqueous calcium and strontium; $\gamma_{Ca}2+$ and γSr^{2+} are the activity coefficients of aqueous Ca^{2+} and Sr^{2+} ions, and $[H_2O]$ is the activity of water. Equation 5 shows that equilibrium values of D depend on three factors (McIntire, 1963): (1) the ratio of the endmember solubility products, which is related to the difference in the standard-state chemical potentials between the aqueous-solution and the solid-solution; (2) a solution interaction factor expressed by the activity of water, the ratios of the aqueous activity-coefficients, and the "speciation" fractions; and (3) a solid-solution-interaction factor expressed by the ratio of solid-phase activity coefficients.

Distribution coefficient values determined in laboratory experiments are typically fairly constant, and vary by less than an order of magnitude, even though the D values determined are not usually representative of equilibrium partitioning. Even D values that do represent equilibrium

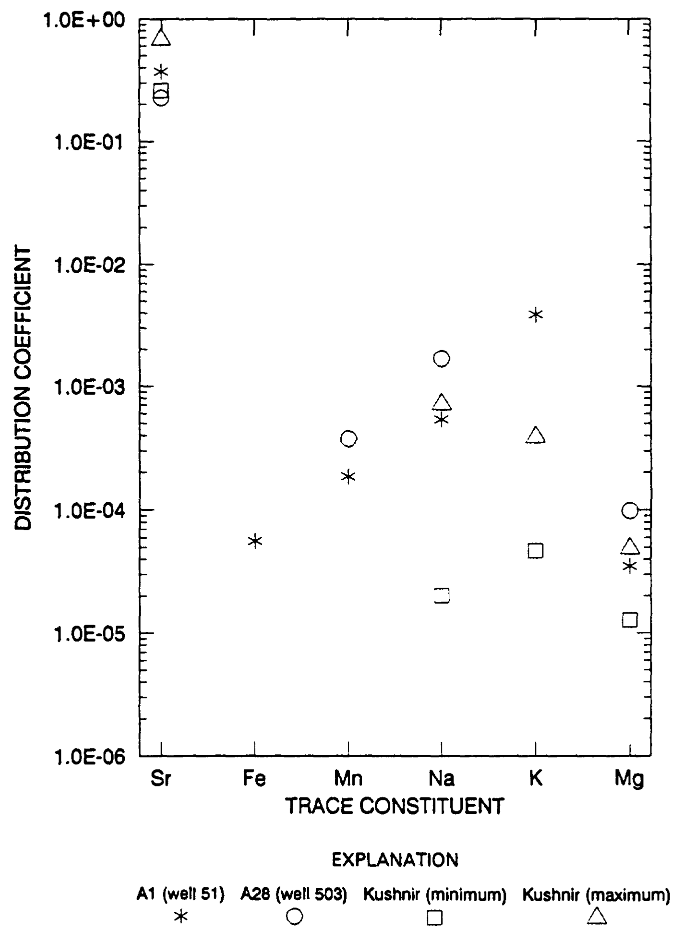

Figure 3. Distribution coefficients for Sr, Fe, Mn, Na, K, and Mg in gypsum collected from the drill cuttings of well 51 and in gypsum precipitated from a sample of well 503 ground water. Minimum and maximum distribution coefficients determined by Kushnir (1980) for gypsum precipitated from evaporating seawater brines are shown for comparison.

conditions should vary as a function of solid and solution composition. Figure 3 illustrates these statements. The D values determined for Sr, Na, and Mg in the gypsum crystals from the drill cuttings of well 51 at Pinal Creek fall within the limits of the highest and lowest D values determined by Kushnir (1980) for gypsum precipitating from Mediterranean Sea brines under various growth rates. The Na and Mg distribution coefficients determined for gypsum precipitating from well 503 are only a factor of 2 higher than Kushnir's highest value. The Sr distribution coefficient for well 503 is close to Kushnir's lowest value. The only distribution coefficient considerably different from those measured by Kushnir (1980) is that for potassium. The K distribution coefficient determined for gypsum from well 51 is one order of magnitude higher than Kushnir's highest value.

The distribution coefficients shown in figure 3 have not been corrected for possible fluid inclusions, which probably are not very important given the great difference in elemental ratios between the analyzed gypsum and the aqueous solutions. For example, the Sr:Na and K:Na ratios are two orders of magnitude higher in the gypsum than in the ground water. An accurate determination of distribution coefficients, however, would require an estimate of fluid inclusions--for example, through chloride determinations (according to Kushnir, 1980, chloride does not substitute significantly in gypsum). Of course, the exact composition of the precipitating solution must also be known. Given the difference in the types of precipitating solutions and environments, the distribution coefficients obtained from the Pinal Creek samples are remarkably close to those obtained by Kushnir (1980). Together with the great difference in element ratios between the aqueous and solid phases, this suggests that the impurities measured in the gypsum samples from wells 51 and 503 are not the result of fluid inclusions, but may instead represent substitutional or interstitial solid-solution impurities.

From the aspect of contaminant transport or more generally of ground-water chemical evolution, the nature of an impurity in a precipitating or recrystallizing solid phase is not as important as its amount. Mole ratios of element concentrations between gypsum and aqueous-solution were calculated in order to determine whether gypsum could constitute an important reservoir capable of retarding the flux of given constituents though the Pinal Creek aquifer. The calculations made assumed a 1-percent gypsum content in the aquifer materials (geologist's logs report as much as 5 percent in somes zones at well 51; see Eychaner and others, 1989), a 30-percent porosity, and an average solid density of 2.65 grams per cubic centimeter.

Tables 5 and 6 show that gypsum in the Pinal Creek alluvial aquifer can constitute an important reservoir of Sr, V, and possibly Mo and Ba relative to the amounts present in ground water. Cd and K concentrations also are relatively high. Other mineral reservoirs, such as Fe and Mn oxyhydroxides, may constitute much bigger reservoirs of impurities than gypsum. For example, it is reported that Cu, Zn, and Ni are scavenged by Mn oxides in core samples from wells 107 and 505 (W.H. Ficklin, U.S. Geological Survey, written commun., 1990).

MASS-BALANCE MODELING

The lack of a sharp pH front in the Pinal Creek alluvial aquifer suggests that pH neutralization by mineral-dissolution reactions is occurring slowly relative to the rate of ground-water flow (Glynn and others, 1991, this Proceedings). Mineral dissolution rates need to be incorporated in any realistic model of contaminant transport at Pinal Creek. The first step in such an approach is to identify clearly the relative importance of each reaction affecting ground water pH. Carbonate dissolution, Fe-hydroxide precipitation, Mn-oxide dissolution, and silicate-mineral dissolution are possible controls on ground-water pH. Compared to the other reactions, the dissolution of silicate minerals is very slow and probably cannot be modeled by assuming equilibrium mass transfer.

In order to determine the importance of silicate-mineral dissolution in the most acidic part of the contaminant plume, mass-balance models were constructed on the basis of the results of the carbonate-rock and gypsum analyses reported in this paper, as well as water-analysis data from August 1987 for wells 51, 402, and 404 (table 7) (Eychaner and others, 1989). For the purpose of the modeling exercise, the assumption was made that well 402 water was the result of reaction between the aquifer materials and water from well 51, the most acidic ground water sampled in the contaminant plume. It was further assumed that the significantly lower chloride content of well

Table 5. *Element ratios between gypsum and ground water for a unit volume of alluvial aquifer at Pinal Creek (direct coupled plasma analyses of gypsum)*

[>, greater than]

Well	Sr	Fe	Mn	Na	K	Mg	Ba
	Constituent						
51 (84/11/08)[1]	11.	0.0016	0.0054	0.016	0.11	0.0010	>70
503 (88/06/16)[2]	4.94	[1]240	.0082	.037	[3].27	.0022	.[1]2.1

[1] Analysis reported in Eychaner and others (1989).

[2] Analysis reported in Brown (1990).

[3] Calculated from analyses reported for well 501. Ground water at well 501 has a chemistry similar to that at well 503.

Table 6. *Element ratios between gypsum and ground water for a unit volume of alluvial aquifer at Pinal Creek (graphite furnace analyses of gypsum)*

[>, greater than]

Well	Mo	Co	Ni	Cu	Cd	Al	V
	Constituent						
51 (84/11/08)[1]	>6.58	0.016	0.086	0.0022	0.18	0.013	2.12

[1] Analysis reported in Brown (1990).

Table 7. *Water analyses*

[From Eychaner and others (1989); constitutent concentrations are in millimoles per liter; RS, redox state index; TDIC, total dissolved inorganic carbon; Sr(x100), strontium concentration times 100]

Well	pH	Ca	Cl	Sr(x100)	Mg	Na	Mn	SO_4	SiO_2	TDIC	Fe	Al	RS
	Constituent or property												
404	7.65	0.998	0.226	0.285	0.535	1.17	0.00182	0.187	0.533	3.74	0.00	0.00	16.1
51	3.74	11.0	9.59	1.48	16.0	9.13	1.37	91.6	1.66	4.16	50.1	9.27	669.
402	4.27	13.5	3.95	2.62	7.82	4.78	1.20	34.4	1.60	4.67	9.67	.371	247.

402 relative to that of well 51 was the result of dispersive mixing of the acid-contaminated water (well 51) with background water of a composition similar to that at well 404. Well 404 is located in the basin fill, the conglomerate aquifer directly below the alluvial aquifer. The composition of these three waters is given above.

Eleven possible mineral reactions were considered to explain the changes in the above 12 constituents or properties: calcite dissolution, dolomite dissolution, albite dissolution, anorthite dissolution, gypsum dissolution or precipitation, silica dissolution or precipitation, $Al(OH)_3$ dissolution or precipitation, MnO_2 dissolution or precipitation, $Fe(OH)_3$ dissolution or precipitation, CO_2 gas and O_2 gas dissolution or exsolution. Sr was the only mineral impurity considered because of uncertainty in the very low Ba content of the analyzed carbonate phases and the silicate minerals. The Sr content of silicate minerals in the aquifer material remains to be determined, and, therefore, average Sr contents of alkali and plagioclase feldspars reported by Deer and others (1963) were used (Model 1). The following Sr stoichiometric coefficients used were: 0.016 for calcite, 0.007 for dolomite, 0.043 for gypsum, 0.5 for anorthite, and 0.5 for albite. These coefficients were determined on the basis of 1 mol (mole) of Ca (or Na) per mineral by multiplying the Sr mass-balance equations by 100 (needed for input into the BALANCE computer model; Parkhurst and others, 1982). Three other stoichiometric coefficients for Sr (F_{Sr}) in albite and anorthite were also tried for the sake of comparison. Models 2 and 3 roughly corresponded to the maximum and minimum Sr contents reported by Deer and others (1963). Model 4 uses the plagioclase Sr content determined by Schultz and others (1989) in their mass-balance models of Sr and Ca in the San Joaquin basin. The four mass-balance models are given in table 8.

Although table 8 separates SiO_2 and $Al(OH)_3$ into two distinct phases, it should be recognized that these components could also be represented by a combination of an amorphous kaolinite phase ($Al_2Si_2O_5(OH)_4$) and/or $Al(OH)_3$. A budget of the moles of protons released/consumed by the redox-independent reactions given in table 8 was constructed to evaluate the potential importance of silicate-mineral-dissolution reactions relative to carbonate-dissolution reactions. The simplifying (but reasonable) assumptions were: (1) 1 mol of calcite dissolution consumes 2 mol of protons (H^+), (2) 1 mol of dolomite dissolution consumes 4 mol of H^+, (3) 1 mol of albite dissolution

Table 8. *Four BALANCE models considering a strontium budget*

[F_{Sr}, stoichiometric coefficient for strontium in feldspar; positive numbers indicate dissolution (in millimoles per liter); negative numbers indicate precipitation or exsolution]

	Model 1 $F_{Sr} = 0.5$	Model 2 $F_{Sr} = 0.75$	Model 3 $F_{Sr} = 0.25$	Model 4 $F_{Sr}=0.2$
Well 51 fraction	0.398	0.398	0.398	0.398
Well 404 fraction	.602	.602	.602	.602
Calcite	6.29	7.54	2.35	.278
CO_2 gas	-7.79	-9.04	-3.85	-1.78
Gypsum	-2.14	-2.14	-2.14	-2.14
SiO_2	-7.20	-4.69	-15.1	-19.22
Albite	.444	.444	.444	.444
$Al(OH)_3$	-10.2	-7.73	-18.1	-22.3
Dolomite	1.13	1.13	1.13	1.13
MnO_2	.654	.654	.654	.654
O_2 gas	2.29	2.29	2.29	2.29
$Fe(OH)_3$	-10.3	-10.3	-10.3	-10.3
Anorthite	3.24	1.99	7.18	9.25

Table 9. *Mass balance for some proton consuming/releasing reactions*

[Negative numbers indicate millimoles of protons consumed per liter of water; positive numbers indicate millimoles released]

Reaction	Model 1 (possible)	Model 2 (least likely)	Model 3 (likely)	Model 4 (preferred)
Silicate dissolution	-27.7	-17.7	-59.2	-75.8
$Al(OH)_3$ precipitation	30.6	23.2	54.3	66.9
Sum of above	2.9	5.5	-4.9	-8.9
Carbonate dissolution	-17.1	-19.6	-9.22	-5.08

consumes 4 mol of H^+, (4) 1 mol of anorthite dissolution consumes 8 mol of H^+, (5) 1 mol of $Al(OH)_3$ precipitation releases 3 mol of H^+. Putting kaolinite in the models instead of $Al(OH)_3$ would not change the number of moles of protons released per mole of aluminum lost from solution.

Table 9 shows that silicate dissolution and $Al(OH)_3$ precipitation can affect pH to the same extent as carbonate-mineral dissolution. At least this could be so if the dissolving feldspars were found to contain relatively low concentrations of Sr, such as those found by Schultz and others (1989). Model 4 is currently the preferred model, at least until further evidence becomes available. The two models with the highest Sr contents (models 1 and 2) would result in the release of protons to the aqueous-solution by silicate dissolution--not a very likely scenario. Furthermore, most feldspar analyses given in Deer and others (1989) did not report Sr concentrations, and, therefore, the average concentration determined from their reported analyses (model 1) could be too high. A fifth model with a lower f_{Sr} value of 0.15 was also tried but could not be solved, because it would have required a greater Ca output than allowed by gypsum precipitation, which itself is fixed by the net SO_4 loss from solution.

Several other possible reactions are also likely to directly or indirectly affect the above H^+ budget--namely, the precipitation of Al by phases other than $Al(OH)_3$ or kaolinite (for example, alunite, $AlOHSO_4$). A complete H^+ budget would also need to consider the various redox reactions responsible for the increase in dissolved Mn and the decrease in dissolved Fe. This has not been done in table 9 because of uncertainty as to the reactions responsible for the decrease in Fe concentrations. The computations show a large O_2 input is needed to balance this decrease in Fe. Such a large input is suspect. Furthermore, the Sr increase between wells 51 and 402, although certainly not a direct result of carbonate dissolution, could be explained by reaction mechanisms other than feldspar dissolution--for example, by ion exchange of Ca for Sr or clay-mineral dissolution. Nevertheless, the above budgets can be useful in determining the minimum number of reactions needed to model the advance of acidic contaminated water in a solute-transport model of the Pinal Creek aquifer (Glynn and others, 1991, this Proceedings). Computation time in such models is highly dependent on the number of chemical reactions simulated.

SUMMARY

The results and conclusions of this study are:

(1) Sr and Na are the dominant impurities in gypsum forming from both acidic and neutralized contaminated ground waters at Pinal Creek.

(2) The distribution coefficients measured for Sr, Na, and Mg in gypsum at Pinal Creek agree with published results for gypsum precipitating from seawater brines.

(3) The total amount of chemical impurities determined in the gypsum from Pinal Creek is too small to affect the thermodynamic stability of the mineral significantly and, therefore, cannot be used to explain the slight but prevalent gypsum supersaturation observed in Pinal Creek ground water.

(4) The amount of Mo, V, Sr, Ba, and Cd impurities in gypsum is relatively high compared to the amounts present in contaminated ground waters at the Pinal Creek site.

(5) The increase in Sr downgradient from the most acidic part of the contaminated aquifer does not appear to be caused by carbonate-rock dissolution. Four possible mass-balance models are constructed on the basis of the assumption that Sr was introduced by feldspar dissolution. These models were used in an effort to find the most significant pH-controlling reactions, which could be introduced in a solute-transport model of the Pinal Creek site.

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SOLID-PHASE VARIATIONS IN AN AQUIFER AS THE AQUEOUS SOLUTION CHANGES, GLOBE, ARIZONA

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ABSTRACT

Copper, manganese, zinc, calcium, aluminum, and sulfate were extracted from solid-phase material in the Pinal Creek aquifer. Sequential extractions were used to reveal phase associations of the above constituents in the coatings of the aquifer material. Grab samples were collected from five split-spoon drill holes in the background and in contaminated areas of the aquifer. The aquifer is contaminated with heavy-metal-laden acid mine water from an adjacent copper mine. Manganese oxides are forming at the water table. Apparently, calcium sulfate is precipitating. On the basis of increasing copper concentrations with time, heavy metals are concentrating on the grains as acidity increases because of the depletion of the aquifer carbonates with the acid water.

INTRODUCTION

Acidic water, containing elevated levels of heavy metals, has contaminated the aquifer that is the source of ground water that discharges to Pinal Creek, near Globe, Ariz., (Eychaner, 1988), (fig. 1). The aquifer consists of unconsolidated alluvium as much as 150 ft (feet) thick that overlies thicker carbonate-cemented conglomerate. The acidic water is neutralized by the calcite, thereby retarding its progress through the aquifer. Copper mining activities in an adjacent granite porphyry deposit since 1903 (Peterson, 1962) has produced the conditions that generate the acid mine water. As the neutralization capacity of the aquifer is exhausted, the acidic water will eventually reach the source of Pinal Creek.

Chemical modeling of the ground water in this aquifer by Stollenwerk and Eychaner (1988) suggests that aluminum and iron compounds are precipitating from the water and forming coatings on the grains of the aquifer material. The acidic water also contains as much as 77 milligrams per liter of manganese (Eychaner and Stollenwerk, 1987), and manganese oxide coatings are visible in Pinal Creek. Chao (1984) describes many techniques for extracting metals using reagents designed to attack a specific phase or coating. Among these are reagents to dissolve carbonate phases, manganese oxides, amorphous iron oxides, and crystalline iron oxides. When applied sequentially, these reagents can provide some indications of the reactions taking place in the aquifer.

The purpose of this study was to determine the distribution of the elements copper, zinc, manganese, iron, aluminum, calcium, and sulfur as sulfate, in a background hole and in three holes in the contaminated zone. In order to evaluate the chemical conditions in the aquifer material, a sampling program was designed to collect samples of the aquifer material at the beginning of, during, and near the end of the contamination. The objectives also included determination of the phase association of each element among the carbonate, manganese oxides, amorphous iron oxide, crystalline iron oxide, and residual phases. The purpose of this paper is to report on the results and significance obtained from chemical examination of the aquifer material. The results for a background hole and three holes in the contamination area are included.

METHODS AND MATERIALS

Holes were drilled and samples were collected at sites 107, 451, and 505. Additional samples were collected from site 451 (hole 453) 1 1/2 years after the original sampling. Background samples were collected from hole 010. Each hole was drilled to a depth of about 75 to 80 ft, and samples were collected at random intervals representative of differences in the aquifer material. Each split-spoon individual sample was dried and sieved through an 80 mesh sieve. Metals were extracted from the -80 fraction of each sample as follows:

1. Approximately 1 gram of sample was placed in a plastic centrifuge tube. Carbonate material was dissolved with 20 mL (milliliters) of 1.0 molar acetic acid-sodium acetate buffer at pH of 5. The tubes were left standing for 1 hour and then capped and agitated for 4 hours. The aqueous phase was separated by centrifuging at 15,000 revolutions per minute for 10 minutes.
2. Manganese oxides were dissolved from the residue of step 1 using 25 mL of 0.1 N (normal) hydroxylamine hydrochloride ($NH_2OH{\bullet}HCl$) and .01 N nitric acid (HNO_3) and shaking for 30 minutes.
3. Amorphous iron oxides were dissolved from the residue of step 2 with 25 mL of 0.25N $NH_2OH{\bullet}HCl$ and .25N hydrochloric acid (HCl) heated to 70 °C (degrees Celsius) in a shaking water bath for 30 minutes.
4. Crystalline iron oxides were dissolved from the residue of step 3 with 25 mL of 4.0N HCl heated to 90 °C for 30 minutes in a water bath.
5. Residual metals were released from the silicate minerals by treating the residue with hydrofluoric, perchloric, and nitric acids and evaporating to near dryness. The resulting product was dissolved in 0.5 N HNO_3.

Total metals were determined using the method of Lichte and others (1987). Metals in the partial extraction solutions were determined by atomic absorption spectrophotometry. Sulfate concentrations for each of the solutions were determined by ion chromatography after chemical interferences were removed with ion exchange precolumns.

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[1] U.S. Geological Survey, Denver, Colo.

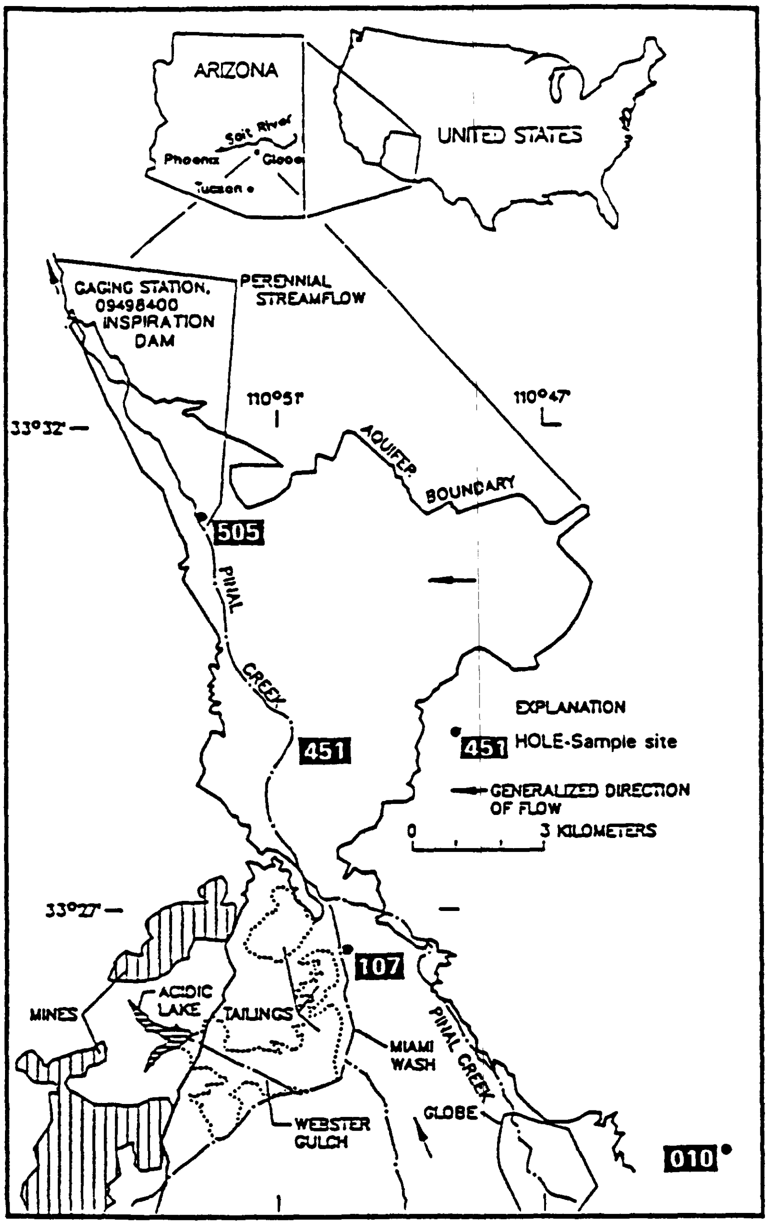
ARIZONA
Salt River
Phoenix
Globe
Tucson
UNITED STATES
GAGING STATION, 09498400 INSPIRATION DAM
PERENNIAL STREAMFLOW
110°51'
110°47'
33°32'
AQUIFER BOUNDARY
505
PINAL CREEK
451
EXPLANATION
451 HOLE-Sample site
GENERALIZED DIRECTION OF FLOW
0
3 KILOMETERS
33°27'
107
MINES
ACIDIC LAKE
TAILINGS
MIAMI WASH
PINAL CREEK
GLOBE
WEBSTER GULCH
010

Figure 1. Map of the study area showing sample collection locations.

RESULTS AND DISCUSSION

Plots of metal concentrations of copper, zinc, and manganese in each hole as a function of depth are presented in figure 2. A manganese anomaly occurs in holes 107 and 505 at depths of 17.5 ft and 0.9 ft respectively. Copper and zinc concentrations are also well elevated above the background (in hole 010) for these sample intervals as well. Most of the manganese at 17.5 ft in hole 107 and at 0.9 ft in hole 505 was extracted by the manganese oxide reagent of Chao (1972) indicating that the manganese occurs as manganese oxide coatings on the grains of the aquifer material. Manganese oxides, excellent scavengers of heavy metals (Chao and Theobald, 1976), are forming at the water table at depths of 17.5 ft in hole 107, at 0.9 ft in hole 505, and possibly at 13 ft in hole 451, and, in turn, are concentrating copper, zinc, and probably other metals in the manganese oxide coatings on the aquifer material.

Concentrations of calcium, aluminum, and sulfate are presented in figure 3. Stollenwerk and Eychaner (1987) predicted that aluminum hydroxy sulfate ($AlOHSO_4$) is one mineral phase that would precipitate from the acidic water. However, the data plots suggest that this is not the case. The extracted aluminum and sulfate concentrations do not correlate. The carbonate extractant dissolved very little aluminum (fig. 3) On the other hand, large concentrations of calcium and sulfate were extracted by the carbonate extraction and positively correlated. Hence, precipitation of gypsum may be one of the controlling reactions for sulfate.

Significant concentrations of copper were extracted from aquifer samples from hole 451 at depths greater than 38 ft by partial extractions (fig. 2). An increase in copper concentration with depth in that hole suggests that the acid mine water flows at depths of 38 to 77 ft or more in this part of the aquifer. Only about 10 percent of the copper in hole 451 between depths of 38 and 77 ft is residual. The copper concentrations in hole 451 are elevated by two to three times higher than those in the background hole (fig. 2), suggesting that labile copper compounds are forming in the aquifer where the acid water has been flowing.

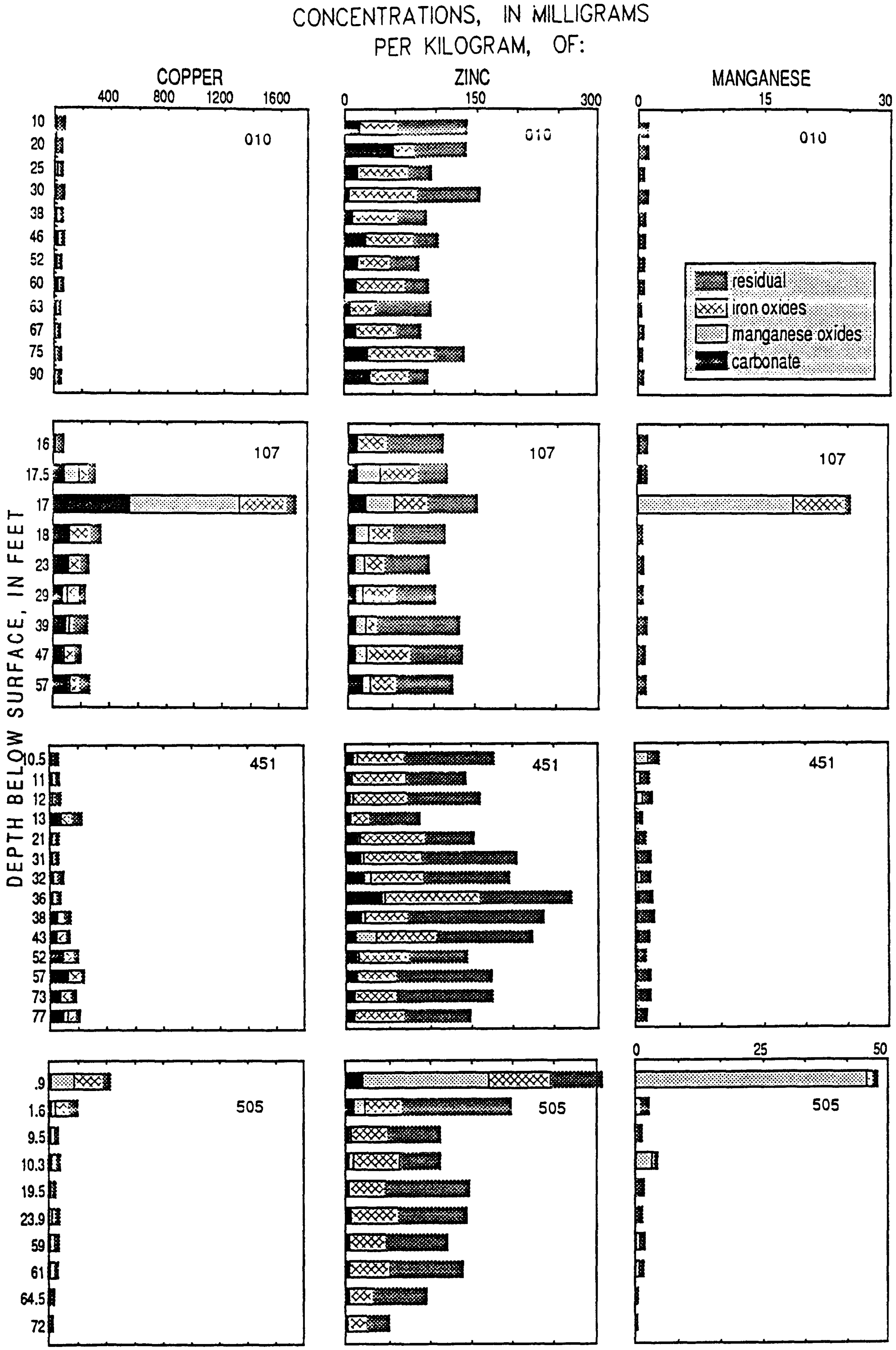

Figure 2. Analytical results for extraction of copper, zinc, and manganese in hole 010 (background), 107, 451, and 505.

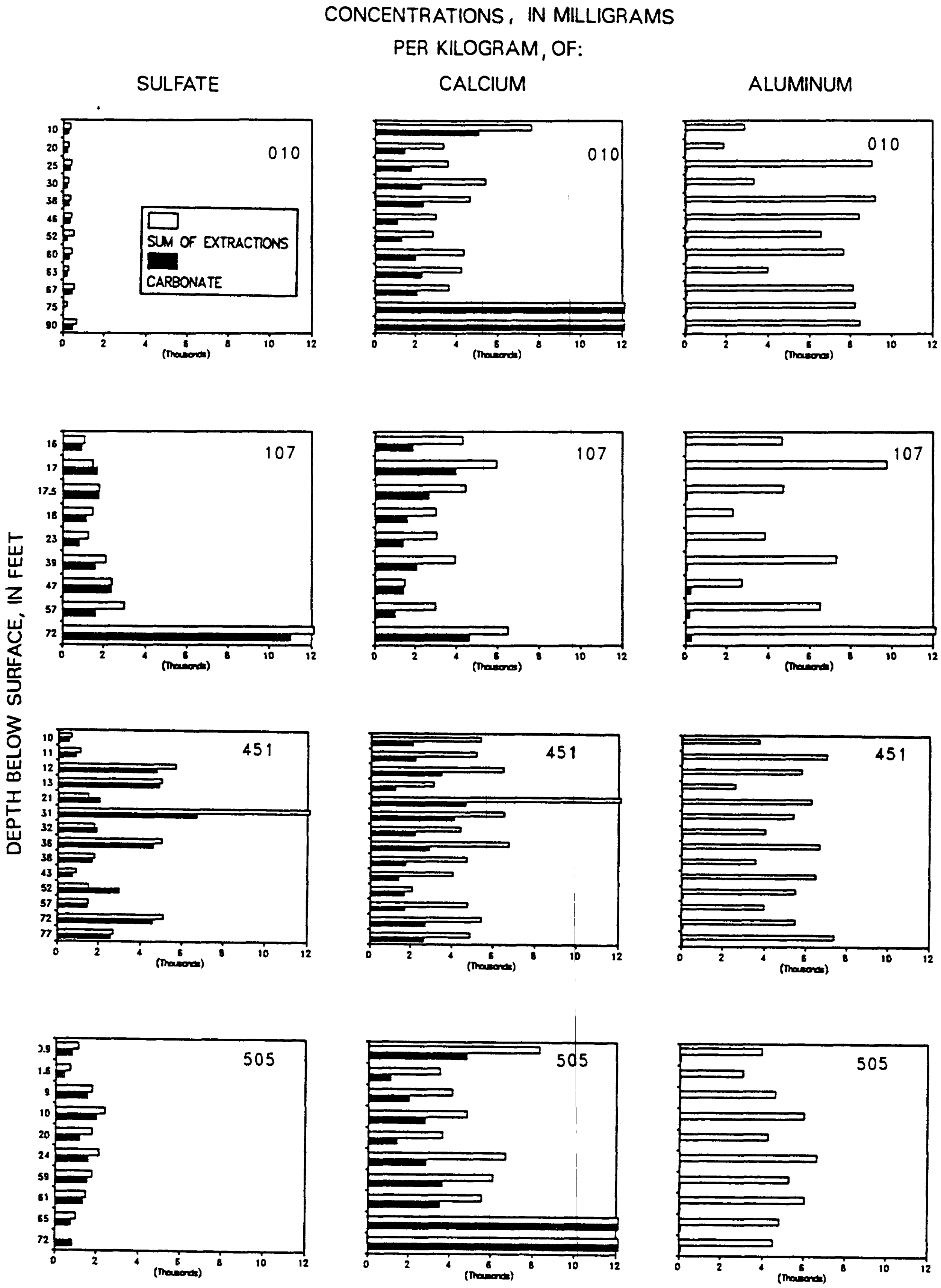

Figure 3. Analytical results for extraction of aluminum, calcium, and sulfate in holes 010, 107, 451, and 505.

The series of partial extractions was applied to a group of samples collected 1 1/2 years later at site 451. Concentrations of copper, zinc, and manganese in the two holes are presented in figure 4. Comparison of copper concentrations in hole 451 in December 1988 to those in hole 451 in May 1990 shows an approximate twofold increase of copper

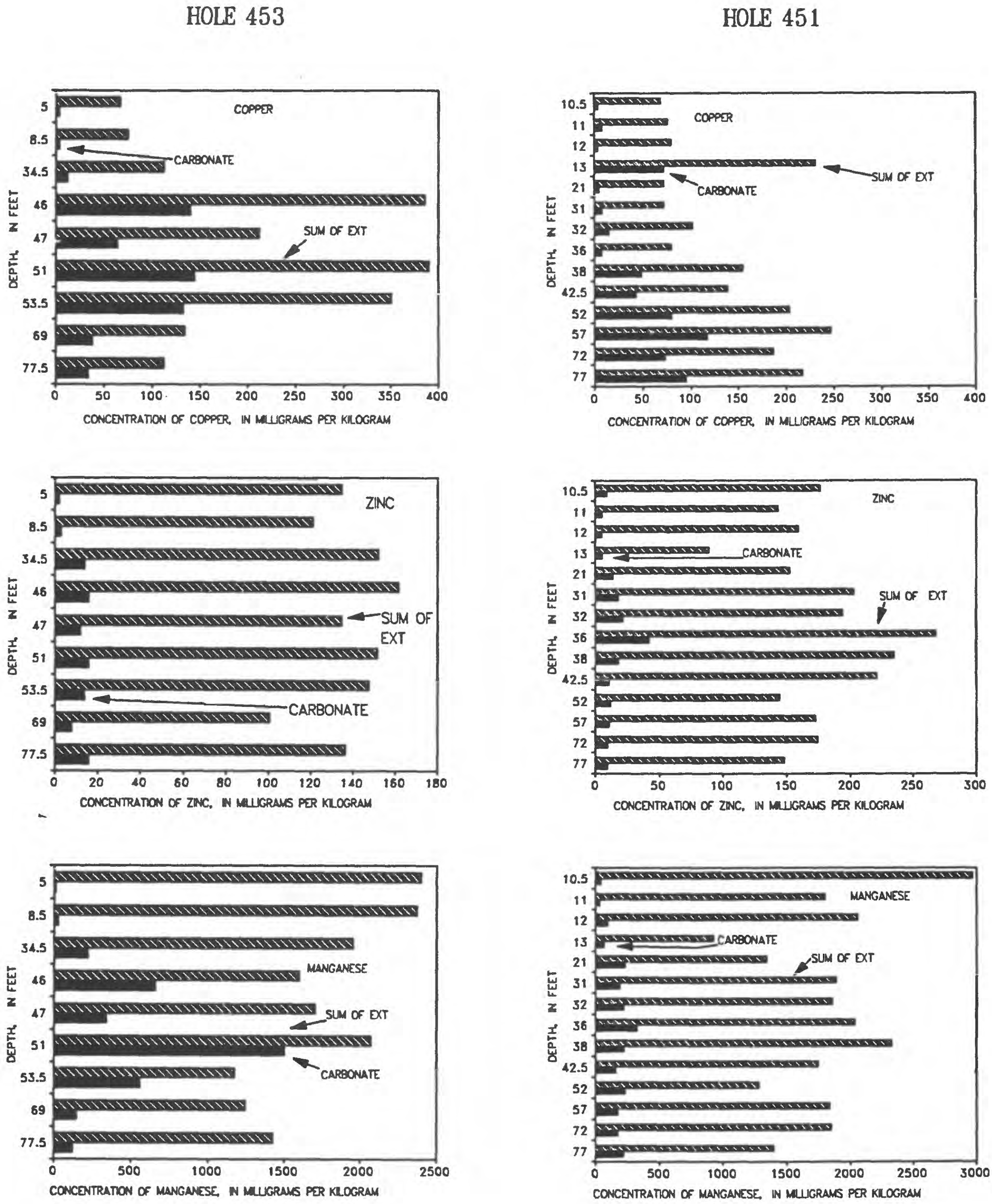

Figure 4. Analytical results for hole 453 and 451 showing changes in concentration of copper, zinc, and manganese from December 1988-May 1990. (Sum of ext represents the sum of the concentrations for all of the extractions).

concentration at depths from about 38 to 77 ft. The increase in copper concentration coincides with a decrease in the pH (from 5 to about 4) of the water at that location (J.H. Eychaner, U.S. Geological Survey, oral commun., 1990) and suggests that copper may be concentrating in the aquifer material over time. The effect is not as noticeable for manganese and zinc; however, the concentration of carbonate-extractable manganese has increased dramatically. The carbonate extraction dissolves exchangeable constituents, and the copper and manganese that dissolved in this extraction may result from ion exhange.

Iron oxyhydroxides are quite likely forming in the aquifer but the data from the partial extractions reveal no particular geochemical associations. Perhaps because the concentration of extractable iron phases in the background samples are almost identical to those in the contaminated samples, and because iron is one of the major constituents of the rock material forming the aquifer, the small addition of iron resulting from reactions of the acidic water cannot be detected.

SUMMARY

Many chemical reactions are occurring in the Pinal Creek aquifer where carbonates in the alluvium are slowly neutralizing the acid mine water. Our data show that formation of manganese oxide coatings occurs at or near the water table where acid mine water enters and exits the aquifer. Gypsum may be precipitating at several locations in the aquifer, and trace-metal concentrations are increasing concurrently with a decrease in pH. The pH decrease coincides with the acidification of the aquifer.

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SOLUTE TRANSPORT IN PERENNIAL STREAMFLOW AT PINAL CREEK, ARIZONA

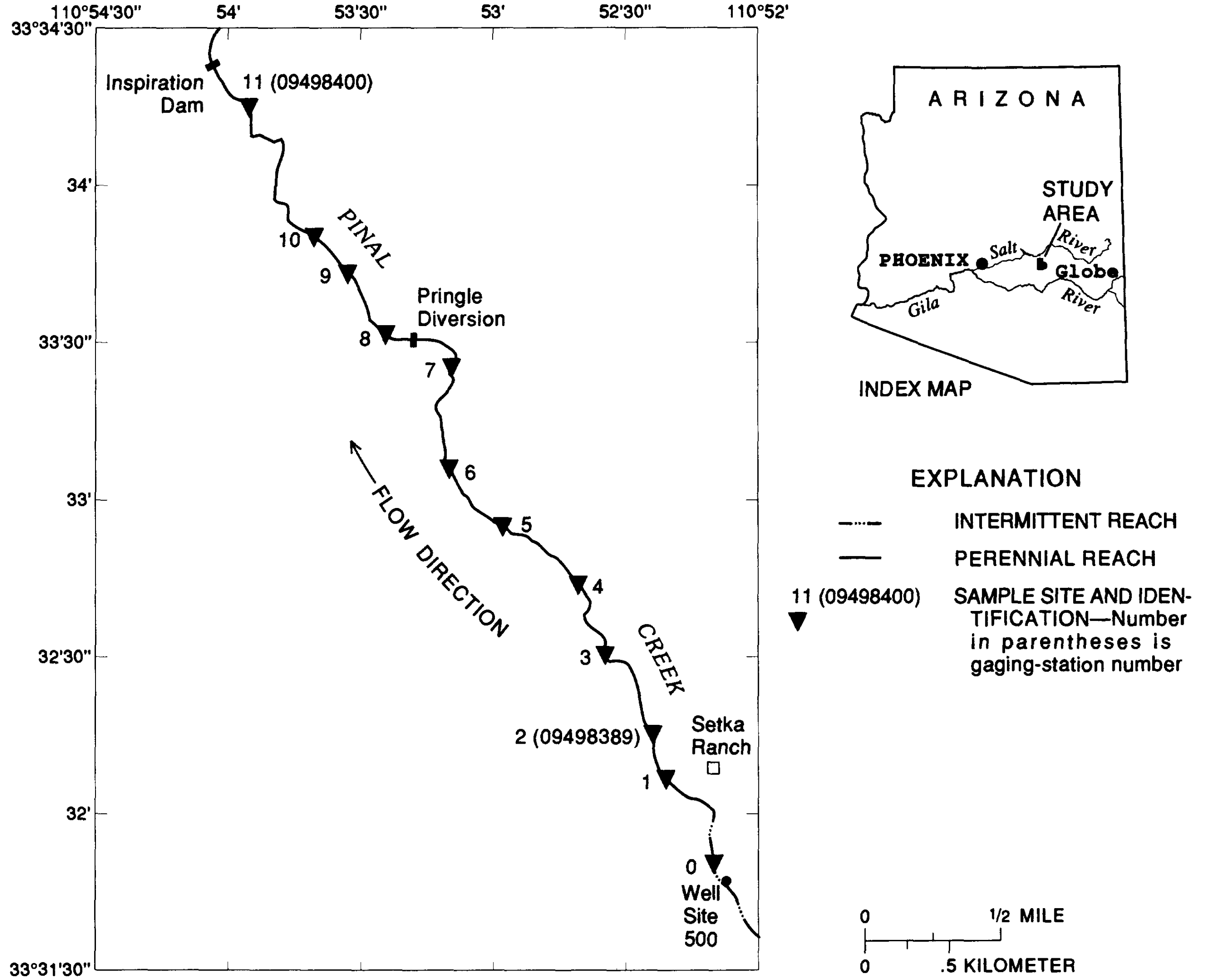
By James H. Eychaner[1]

ABSTRACT

Black manganese oxide precipitates in a 6-kilometer-long perennial flow reach of Pinal Creek. Samples collected March 6-8, 1990, from streamflow and shallow ground water at 11 sites showed that, through the reach, pH increased 1.5 units, Manganese decreased 80 percent, and dissolved inorganic-carbon concentration decreased 45 percent. A conservative-mixing model using only ground-water analytical concentrations adequately represented most constituents in streamflow. A reaction-path model using the computer program PHREEQE specified carbon dioxide degassing, manganese precipitation, and calcite dissolution to represent pH, Manganese, and inorganic-carbon trends. The model could be improved by considering details of carbon dioxide degassing, ion exchange, gypsum and silica reactions, diurnal variation in reaction rates, and biological activity.

INTRODUCTION

During 1988-89, ground water at well site 500 near the head of perennial flow in Pinal Creek (fig. 1) had a pH of 5.7 to 6.1 and contained 40 to 60 mg/L (milligrams per liter) of dissolved manganese (Mn), less than 1 mg/L dissolved oxygen (DO), and about 110 mg/L dissolved inorganic carbon (DIC). At the same time through a 6-km (kilometer) long perennial flow reach downstream, concentrations of DIC decreased and DO increased toward atmospheric equilibrium, pH increased about 1.2 units, and dissolved Mn decreased 35 to 65 percent. Abundant black Mn-oxide precipitates cemented the alluvial streambed in the reach. Streambed sediments, however, provide only a temporary sink for Mn because flood discharges break up and transport the weakly cemented sediments.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32'
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Inspiration Dam
11 (09498400)
10
9
PINAL
Pringle Diversion
8
7
6
FLOW DIRECTION
5
4
CREEK
3
2 (09498389)
Setka Ranch
1
0
Well Site 500
ARIZONA
STUDY AREA
PHOENIX
Salt
River
Globe
Gila
River
INDEX MAP
EXPLANATION
INTERMITTENT REACH
PERENNIAL REACH
11 (09498400)
SAMPLE SITE AND IDENTIFICATION—Number in parentheses is gaging-station number
0
1/2 MILE
0
.5 KILOMETER

Figure 1. Area of study and sites sampled March 6-8, 1990.

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[1] U.S. Geological Survey, Honolulu, Hawaii.

During March 6-8, 1990, streamflow samples were collected at 11 sites in the perennial reach of Pinal Creek in order to evaluate the interactions among pH, Mn precipitation, and gas exchange with the atmosphere as well as other processes (fig. 1). Ground-water samples were collected at the 11 sites and at a 12th site upgradient from the beginning of surface flow.

This paper presents conservative-mixing and reaction-path models for streamflow concentrations of major constituents, Mn, and DIC measured during the experiment. Faires and Eychaner (1991, this proceedings) present information on temporal and spatial trends of trace elements in the same reach, and Eychaner (1991, this proceedings) describes the study area and overall project objectives.

METHODS

Sites were selected along the stream at intervals of 250 to 1,160 m (meters) to sample the expected variations of discharge and chemistry; the exact points were selected in the field on the basis of channel characteristics and accessibility (fig. 1). Sites 2 and 11 were at the locations of previous periodic sampling, Pinal Creek at Setka Ranch and Inspiration Dam, respectively.

Samples were collected with a peristaltic pump connected to a nylon sediment-sample nozzle fixed near the centroid of streamflow or to an adjacent 1.9-cm (centimeter) diameter stainless-steel well casing. Wells had stainless-steel wire-wound screens 30 cm long with openings 0.025 cm wide, were driven by hand to about 1.5 m below the water table, and were developed by pumping for 10 to 20 minutes. Sample water was pumped without atmospheric contact through a cell in which pH, temperature, DO, specific conductance, and platinum (Pt) electrode potential were measured. Alternatively, the water was pumped through a 0.45-micrometer filter or directly to sample bottles. Reusable equipment was rinsed thoroughly with streamwater between uses, followed by a final rinse with commercial deionized water.

Samples for major dissolved constituents were analyzed by K.G. Stollenwerk (U.S. Geological Survey, Lakewood, Colo.,) using inductively coupled plasma-Qatomic emission spectrometry and other methods. DIC samples were analyzed by the U.S. Geological Survey National Water-Quality Laboratory. Replicates and field blanks were analyzed.

Stream discharge was measured by current meter, and temporary staff gages were installed. About 40 percent of the discharge from the aquifer occurred in the first 0.6 km of streamflow (Faires and Eychaner, 1991, this proceddings, fig. 2). Streamflow temperature, DO concentration, pH, and specific conductance were recorded bihourly at four sites. Atmospheric pressure, temperature, relative humidity, and windspeed were recorded at one site and measured at each site during sample collection.

The geochemical computer program PHREEQE (Parkhurst and others, 1985) was used to compute elemental speciation in solutions, saturation indices with respect to selected minerals, and results of mass transfers between minerals and solutions. Streamflow ionic strength was about 0.06 mole per liter.

CONSERVATIVE-MIXING MODEL

Discharge in the study reach was steady throughout the sample period. Analysis of 17 discharge measurements and 77 gage-height observations indicated that discharge varied less than 10 percent at each site. The last previous increase in discharge caused by precipitation had been about 7 weeks earlier.

Temperature and DO concentrations varied diurnally in the streamflow, and the diurnal range of each increased downstream (fig. 2). Average temperature decreased downstream by about 0.4 °C (degrees Celsius) per kilometer

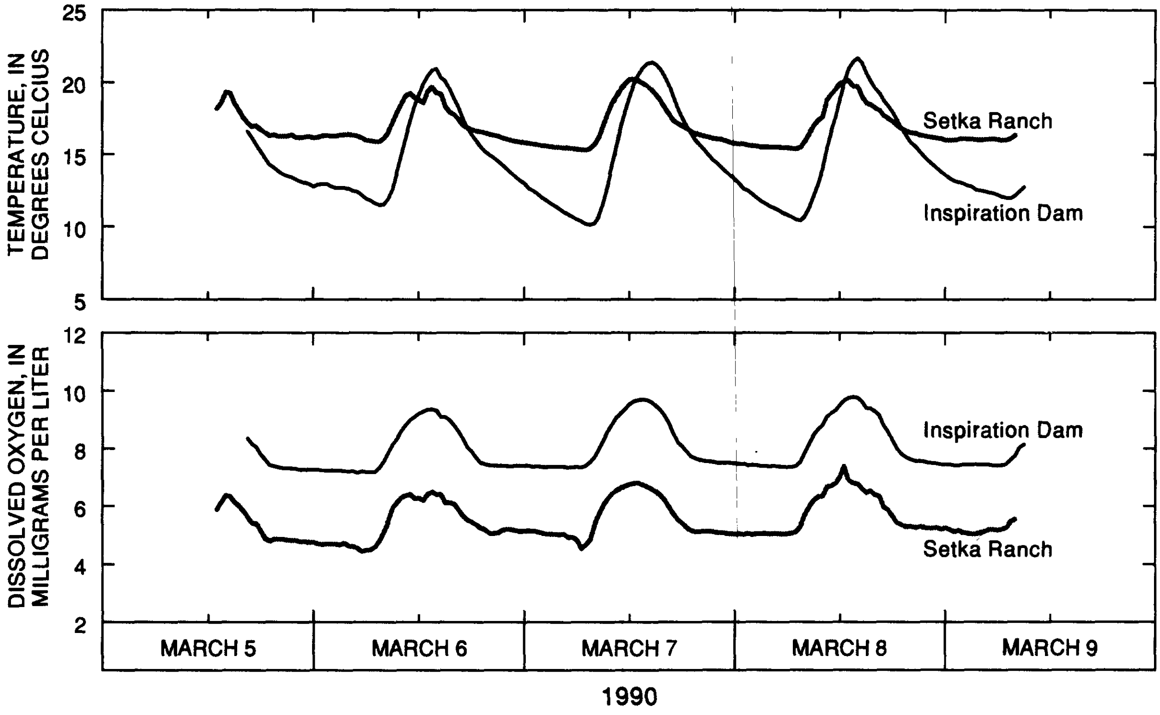

Figure 2. Diurnal variation of streamflow temperature and dissolved-oxygen concentration.

but remained 4.5 °C above average air temperature after 5 km. Average DO was 5.6 mg/L after the initial 0.7 km of flow and increased downstream by about 0.5 mg/L per kilometer. Abundant algae in the creek contributed to DO variations. Diurnal variations of pH and specific conductance were small.

Six additional streamflow samples were collected at five sites from 6 to 27 hours before or after the major sampling; analytical concentrations of all nonvolatile constituents varied less than 10 percent at each site (fig. 3). Therefore, the system was analyzed as being chemically at steady state.

A trend line of concentrations for dissolved silica (SiO_2) in the streamflow decreased about 20 percent of its mean through the reach; magnesium (Mg) and sulfate (SO_4) decreased about 10 percent; chloride (Cl) decreased 6 percent; and sodium (Na) and calcium (Ca) increased about 1 percent (Faires and Eychaner, 1991, this proceedings, fig. 5). In contrast, DIC decreased from 29 to 16 mg/L, pH increased from 6.0 to 7.5, and Mn decreased from 90 to 15 mg/L.

For ground water, the concentration-trend lines decreased 12 to 20 percent of the mean through the reach for Na, Ca, Mg, Cl, and SO_4; the trend for SiO_2 decreased 45 percent. Average DIC was 54 mg/L in the upstream half of the reach and 44 mg/L in the downstream half. At the upper five sites, pH ranged from 5.8 to 6.1 and Mn exceeded 50 mg/L. At the lower five sites, pH generally was between 6.5 and 6.8 and Mn generally was less than 0.3 mg/L.

Conservative mixing was modeled as a cumulative mass balance:

$$C_{S2} = \{C_{S1} Q_{S1} + 0.5(C_{G1} + C_{G2})(Q_{S2} - Q_{S1})\}/Q_{S2}, \quad (1)$$

where C is constituent concentration; Q is discharge; and subscript S refers to streamflow, G to ground water, 1 to the upstream end of a subreach, and 2 to the downstream end. Using ground-water analytical concentrations only, this simple model adequately represented most constituents in streamflow (fig. 4), including constituents that would be expected to react but varied only slightly in the reach.

The mixing model diverged from observed concentrations, however, for dissolved gases and Mn (fig. 5). DIC in the model was about 2.5 times greater than observed, and DO was less than 10 percent of observed concentrations. Model Mn was close to observed concentrations at the beginning of the reach but was three times too large 5 km downstream.

REACTION-PATH MODEL

The partial pressure of carbon dioxide (pCO_2) in streamflow samples decreased from $10^{-1.4}$ to $10^{-2.7}$, and the saturation index (SI) for calcite increased from -1.6 to 0.2 through the study reach. Average SI was 0.04 for gypsum and -0.22 for amorphous silica; no trend was evident. Using Pt electrode potential to estimate pE, SI generally was less than -2 for Mn oxides, although in fact Mn oxides form in the reach; SI was about 1 for rhodochrosite. Mn in aged fine particles of the Pinal Creek streambed can be represented as

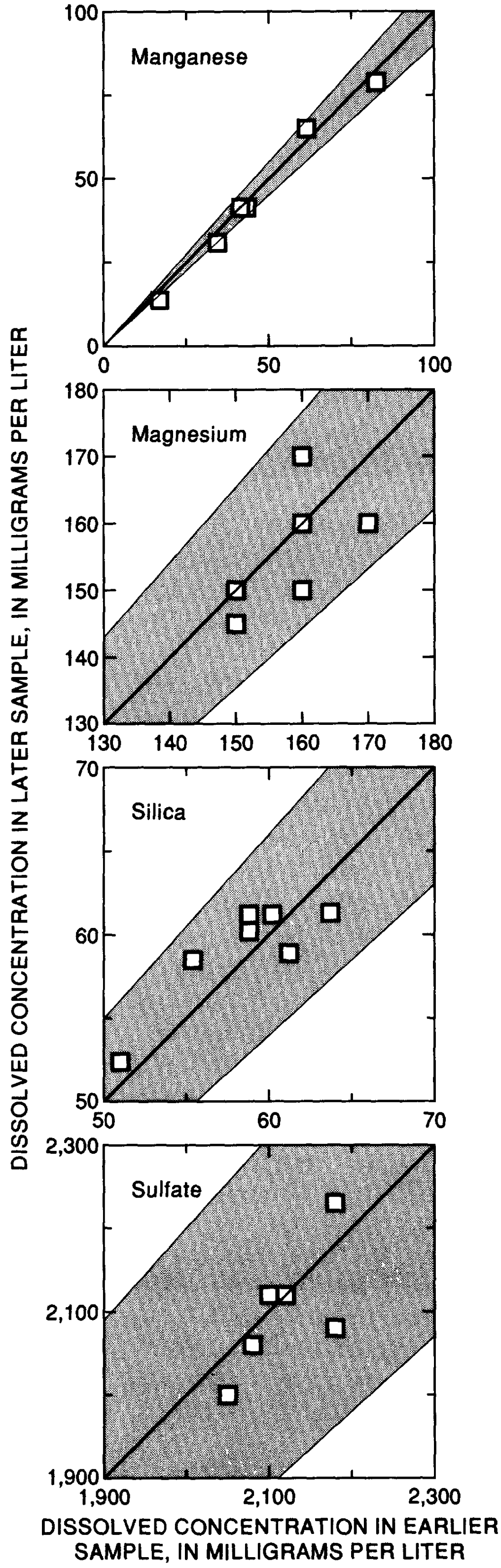

Figure 3. Concentrations of manganese, magnesium, silica, and sulfate in repeated samples from Pinal Creek (area within 10 percent of equal value is shaded).

$(Mn^{[III]}_{0.85}Ca_{0.15})Mn^{[IV]}_4O_9{\bullet}3H_2O$ although several minerals were present (Lind, 1991, this Proceedings); thermodynamic data for this form are not available.

Reaction paths were computed with PHREEQE to develop the simplest possible model that adequately represents observed changes in the streamflow. The model began with the same proportions of ground water as in the conservative-mixing model, and three additional processes were simulated. Reaction amounts given in this section are based on 1 kilogram of solution and are stated in terms of distance because traveltime through the reach is uncertain.

First, net degassing of 5,360 μmol (micromoles) of CO_2 was specified in amounts that decreased linearly from subreach 1 to 6 and continued, at a smaller rate of decrease, to subreach 11. The average rate was 900 μmol/km. Second, Mn precipitation as

$$4.85Mn^{2+} + 0.15Ca^{2+} + 9H_2O = (Mn_{0.85}Ca_{0.15})Mn_4O_9(s) + 18H^+ + 8e^- \quad (2)$$

was specified at 30 μmol/km for the mineral. Oxidation of $Mn^{[II]}$ to $Mn^{[IV]}$ was balanced by adding DO at twice the amount of reaction 2. Third, dissolution of calcite,

$$CaCO_3(s) + 2H^+ = Ca^{2+} + H_2CO_3 \quad (3)$$

was specified at 135 μmol/km to offset protons produced by reaction 2. An equal amount of CO_2 degassing maintained the net downstream decrease in DIC. In the absence of Mn precipitation, the observed pH, pCO_2, and calcite SI would result in dissolution of 30 μmol of calcite in the reach, or 5 μmol/km. The amount of each reaction was calibrated to match observed streamflow pH, Mn, and DIC.

The reaction-path model adequately represented observed streamflow by using reasonable amounts of likely reactions (fig. 5). The model reproduced the calcite SI of streamflow samples, which indicates the specified dissolution was reasonable. Simulated Ca concentration varied less than 3 percent through the reach; the differences from observed concentrations were too small to require additional reactions. Average model SI was 0.04 for gypsum and -0.23 for amorphous silica.

Model SI for all Mn oxides exceeded 3 and increased downstream. SI for hausmanite (Mn_3O_4) exceeded 9 for subreaches 10 and 11. The large difference from the SI computed from samples was primarily the result of using simulated pE rather than Pt electrode potential. The logarithmic ion-activity product for reaction 2, for example, depends more sensitively on pH and pE than on Mn activity.

The reaction-path model represents the trend of changes along the perennial reach of Pinal Creek, but no attempt was made to represent details in each subreach. Particularly in the four upstream subreaches (fig. 1), where the proportion of ground-water inflow is greatest and pH and dissolved-gas concentrations change most rapidly, a different combination of reactions or amounts could improve the results; ion-exchange reactions might be significant.

For the entire reach, reactions involving gypsum and amorphous silica are likely but probably small. Further analy$is could improve the specification of CO_2 degassing as a function of pCO_2 and subreach length. Finally, diurnal variations in reaction rates caused by temperature, illumination, DO, or biological activity could be considered.

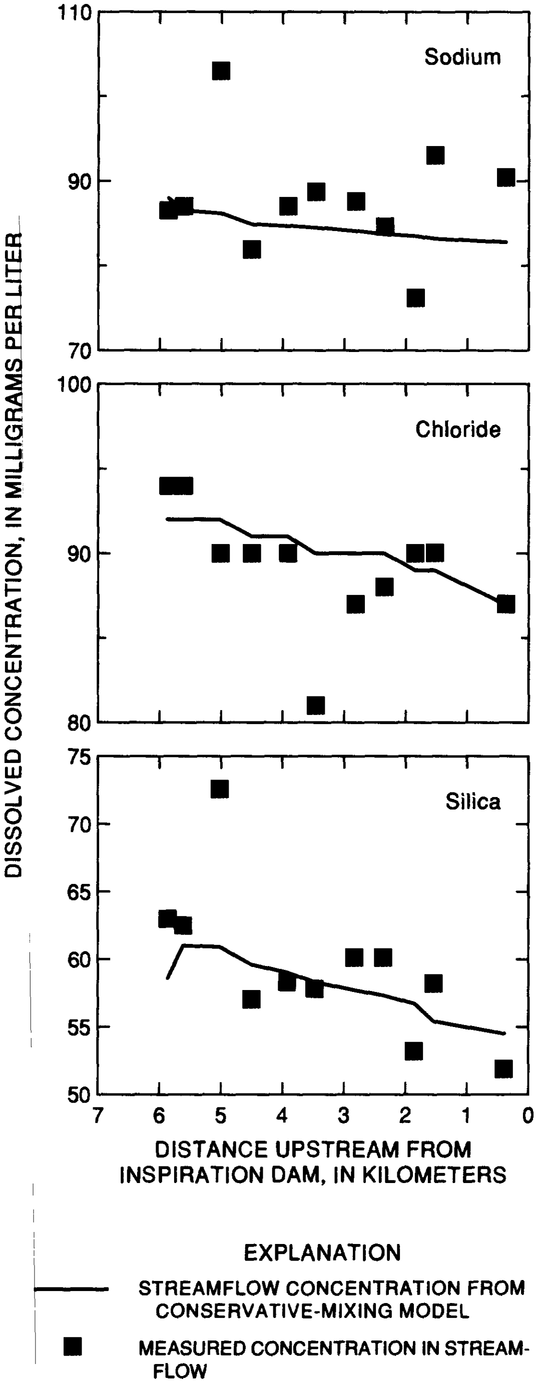

Figure 4. Concentrations of sodium, chloride, and silica in water samples and the conservative-mixing model.

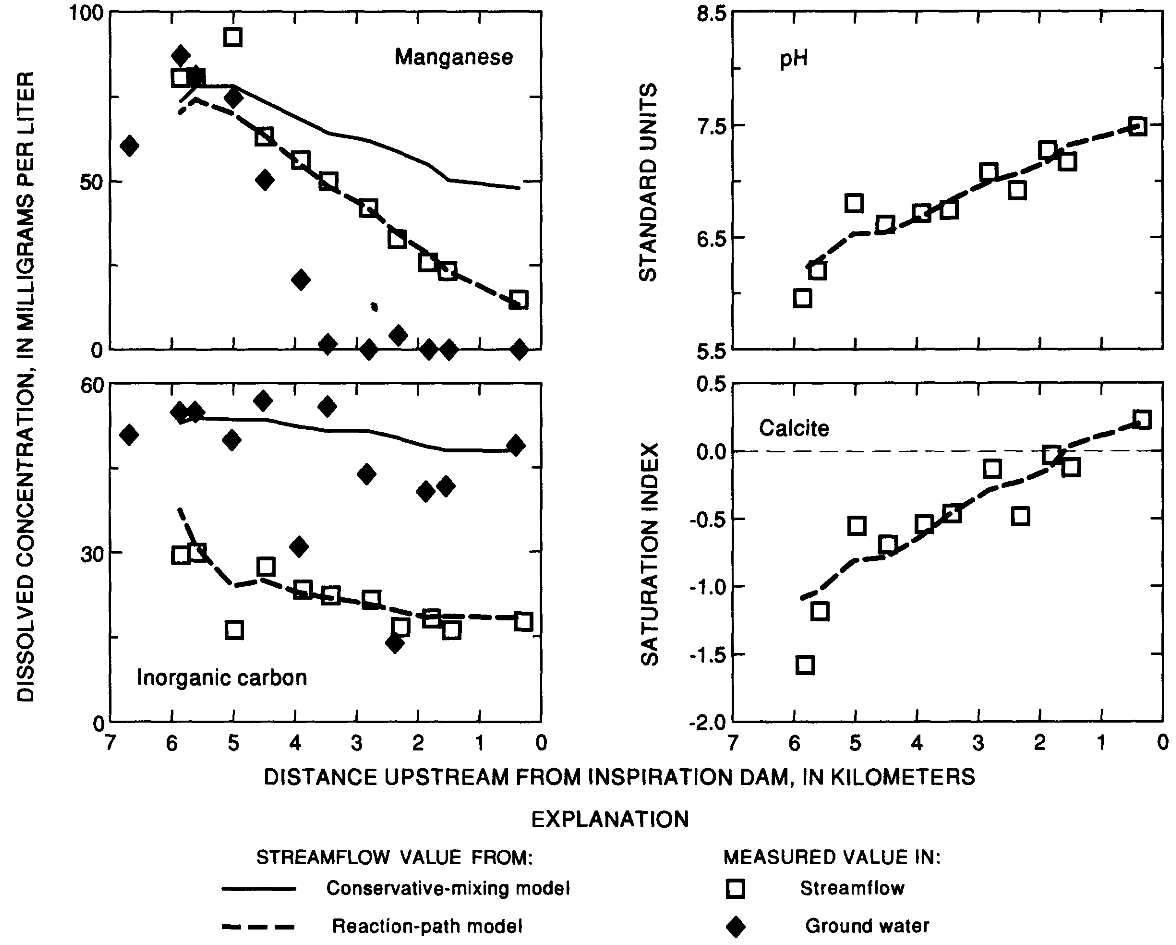

Figure 5. Concentrations of manganese and inorganic carbon, pH, and calcite saturation index.

SUMMARY

Black Mn-oxide precipitates have been observed to cement the streambed of Pinal Creek in a 6-km-long perennial-flow reach. Samples collected in March 1990 from streamflow and shallow ground water at 11 sites in the reach showed that pH increased 1.5 units, Mn concentration decreased 80 percent, and DIC decreased 45 percent. The system was analyzed as being chemically at steady state because discharge and measured chemical concentrations varied less than 10 percent at each site during the study. A conservative-mixing model using only measured ground-water concentrations adequately represented most constituents in streamflow.

A reaction-path model was calibrated to observed DIC and Mn concentrations and pH using PHREEQE. The model specified average CO_2 degassing of 900 μmol/km per kilogram of solution, precipitation of 30 μmol/km of an identified Mn oxide mineral from Pinal Creek, and calcite dissolution of 135 μmol/km. The model represented trends along the reach but not subreach details. The model could be improved by considering CO2 degassing in greater detail, ion exchange, gypsum and silica reactions, diurnal variation in reaction rates, and biological activity.

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MANGANESE MINERALS AND ASSOCIATED FINE PARTICULATES IN THE PINAL CREEK STREAMBED

By Carol Lind[1]

ABSTRACT

Recently formed black manganese crust from the Pinal Creek streambed was sized and the magnetic and nonmagnetic parts of each fraction were segregated. Hot hydrochloric acid extraction showed that the iron to manganese molar ratios were 5 to 10 in the 150- to 250-micrometer particles but were much less than 0.1 in the nonmagnetic fractions of the 150- to 250-micrometer particle surface-layers, the 0.1- to 10-micrometer particles washed off the 150- to 250-micrometer particles, and the sieved 0.1- to 10- micrometer particles. Chemical analysis and x-ray diffraction information suggest a mixture of $(Ca,Mn^{2+})Mn^{4+}{}_4O_9$*-hydrate and* $(Mn^{2+},Ca)Mn^{4+}{}_4O_9$*-hydrate. The identity of the carbonate is questionable. Of the patterns for the carbonate mineral(s) that might be present, the x-ray diffraction pattern for calcian kutnahorite* $(Ca_{0.74}(Mn,Mg)_{0.26}CO_3)$ *matched the sample pattern best. X-ray diffraction patterns of particles from which manganese solids were removed indicated the presence of plagioclase, quartz, and lesser amounts of mica and chlorite. The manganese oxides obscured the plagioclase and the chlorite in the less-than-75-micrometer fractions.*

INTRODUCTION

In the Pinal Creek watershed, acidic seepage from copper mining (pH about 2.7) alters the chemistry of Pinal Creek. The subsurface water, acidified by this seepage, reacts with the alluvium through which it passes and precipitates metals as it is gradually neutralized by interaction with calcite. As the alluvium buffering capacity is consumed, acid water moves downstream preceded by the water that has interacted with calcite. Iron oxides precipitate where the water is partially neutralized and farther downstream, well in advance of the acid front, manganese crusts develop where the water is near neutral. These black crusts were first observed in 1985 in the streambed at sampling station 09498400 at Inspiration Dam (fig. 1). If the front continues to advance at its previous rate over the next 5 to 10 years, the crust would be expected to change to an iron oxide (Eychaner, 1989, p. 570-572).

This paper identifies the mineral composition of the manganese crusts before they are altered by changes in stream chemistry. Identification of the minerals associated with the streamwater is crucial to understanding and modeling the stream chemistry.

SAMPLE PREPARATION

Black crust was wet-sieved with simulated Pinal Creek water through stainless-steel screens and the magnetic and nonmagnetic parts of the less-than-250-μm (micrometer) fractions were segregated. The sediment was separated into 0.1- to 38-, 38- to 43-, 43- to 65-, 65- to 75-, 75- to 150-, and 150- to 250-μm size fractions. Original ion-solid relations were strengthened by separation of the suspendable, nonmagnetic material from the coarser less-than-250-μm sediment using Pinal Creek water that had been filtered through 0.1- μm Nuclepore[2] filter paper. Further segregation of the finest particles was attempted by settling some of the less-than-38-μm fraction in water and some in acetone.

METHODS

The mineral identifications involved determination of the amount and oxidation state of the manganese oxides in the size fractions high in manganese, determination of the associated major-cation-to-manganese molar ratios of these oxides and x-ray diffraction (XRD) examination of all fractions of the less-than-250-μm sediments and of aliquots of specially treated, high-manganese sediment fractions. Mineral identities were deciphered by graphic comparison of these XRD patterns with Joint Committee on Powder Diffraction Standards (JCPDS) data using the Nicolet computer programs.

The size fractions containing high manganese concentrations were identified by atomic adsorption spectrometric (AAS) analysis of leachates from sediment fractions that had been heated to near boiling temperature in Ultrex hydrochloric acid (HCl).

Oxidation numbers were determined by the oxalate-sulfuric acid method (Hem, 1980, p.55). Ultrex sulfuric acid was used so that the remaining untitrated oxalate-sulfuric acid leachate could be analyzed for cations by AAS.

In the high-manganese sediment fractions, the XRD identification of manganese oxides was facilitated by the removal of carbonate mineral(s) and exchangeable cations with ammonium acetate/acetic acid buffer of pH 4.5 (Gatehouse and others, 1977), and the XRD identification of nonmanganese minerals was facilitated by gentle reduction of the manganese oxides with ascorbic acid in a sodium acetate/acetic acid buffer (pH near 4). The solids from these two extractions were separated from their leachates by filtration using 0.1-μm Nuclepore filters and were washed with distilled, deionized water.

CHEMICAL ANALYSIS

The iron-to-manganese molar ratios of sediment leachates that had been maintained in HCl at near boiling temperature for several hours were as follows: the 150- to 250-μm magnetic fraction, near 10; the 150- to 250-μm nonmagnetic fraction, greater than 5; the 0.1- to 10-μm suspended material washed off the 150- to 250-μm nonmagnetic fraction, 0.02; and the 0.1- to 10-μm sieved fraction, 0.03. The iron-to-manganese molar ratio of the

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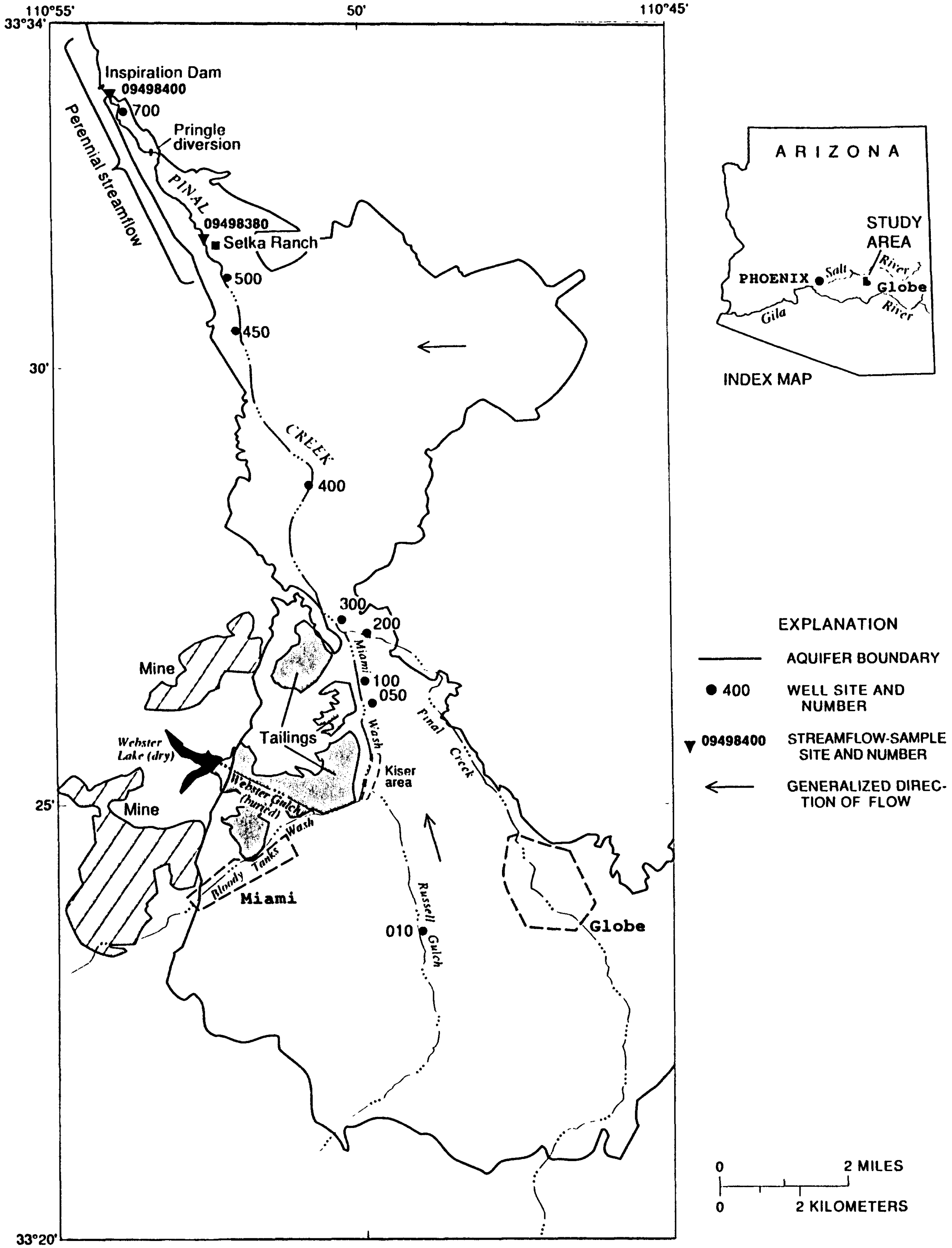
[1] U.S. Geological Survey, Menlo Park, Calif.

[2] Use of firm, brand, or trade names in this paper is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.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Inspiration Dam
09498400
700
Pringle diversion
Perennial streamflow
PINAL
09498380
Selka Ranch
500
450
CREEK
400
300
200
Mine
Miami
100
050
Wash
Pinal
Creek
Tailings
Webster Lake (dry)
Kiser area
Webster Gulch (buried)
Mine
Wash
Bloody Tanks
Miami
Russell
Gulch
010
Globe
ARIZONA
STUDY AREA
PHOENIX
Salt
River
Globe
Gila
River
INDEX MAP
EXPLANATION
AQUIFER BOUNDARY
● 400 WELL SITE AND NUMBER
▼ 09498400 STREAMFLOW-SAMPLE SITE AND NUMBER
← GENERALIZED DIRECTION OF FLOW
0
2 MILES
0
2 KILOMETERS

Figure 1. Map showing sampling site at Inspiration Dam, mines, tailings, former acid lake, and both the perennial and the intermittent flow path of Pinal Creek.

150-to 250-µm nonmagnetic fraction that had been maintained in HCl at near boiling temperature for only 5 to 10 minutes was 0.08. Evidently, iron predominates considerably over manganese inside the large particles. In contrast, manganese predominates over iron in the surface layers of the nonmagnetic large-particles; in the nonmagnetic fine particulates attached to the large particles; and in the nonmagnetic very fine suspendable particles.

The small sized particles consisted almost entirely of manganese solids as shown by the barely perceptible residues left after the ascorbic acid reductions of ~20 milligram samples of less-than-75-µm sized fractions. The manganese solids in the less-than-75-µm size particles had an average manganese oxidation number of 3.65 ± 0.04 and could be represented by a manganese oxide with a manganese-oxygen distribution of $(MnO)_{0.85}(MnO_2)_4$. The cation-to-total manganese molar ratios for the oxalate-reduced oxides in the less-than-75-µm fractions averaged as follows: iron, 0.06; calcium, 0.3; magnesium, 0.03; and sodium, 0.045. If the oxide contains all the sample divalent manganese and only calcium as the other divalent ion, a solid consisting of $(Mn_{0.85}Ca_{0.15})Mn_4O_9$ could be present. A mineral series with varying ratios of calcium-to-divalent-manganese, represented by takanelite $(Mn^{2+}{}_{0.89'},Ca_{0.23'},Mg_{0.03})Mn^{4+}{}_{3.94}O_{9.00}.(3H_2O)$ (Nambu and Tanida, 1971) or $(Mn^{2+},Ca)Mn^{4+}{}_4O_9.(3H_2O)$ (Joint Committee on Powder Diffraction Standards, pattern 25-164) and rancieite $(Ca,Mn^{2+})Mn^{4+}{}_4O_9.(3H_2O)$ (Richmond and others, 1969; Joint Committee on Powder Diffraction Standards, pattern 22-718) could have a manganese oxidation number ranging from 3.60 to 4.00.

MINERAL COMPOSITION

Manganese Minerals

In the unaltered sediment, particularly in the less than 75-µm size fractions, a more highly oxidized manganese oxide was suggested by XRD peaks just above 7 Å, at 2.50 Å and less, and at ~1.46 to 1.41 A. Settling the less-than-38-µm particles in acetone enhanced these peaks. Evidently, the acetone oriented the manganese solids so that the other minerals did not overshadow the XRD patterns for the oxide. The XRD patterns of the less-than-75-µm solids from which the carbonate mineral(s) and the extractable cations had been removed consisted almost entirely of peaks representative of the solids, rancieite $((Ca,Mn)Mn_4O_9\cdot(3H_2O))$ and a similar more hydrated structure $((Mn,Ca)_3Mn_{12}O_{27}.(15H_2O))$ (Joint Committee on Powder Diffraction Standards, patterns 22-718 and 4-149, respectively) (fig. 2). In rancieite, the calcium-to-divalent-manganese molar ratio is greater than 1 and, in the more hydrated structure and in takanelite, this ratio is less than 1. The more hydrated structure could be part of the suggested mineral series or it may be a distinct crystal identity. Wadsley (1950) prepared this oxide in an aqueous solution at

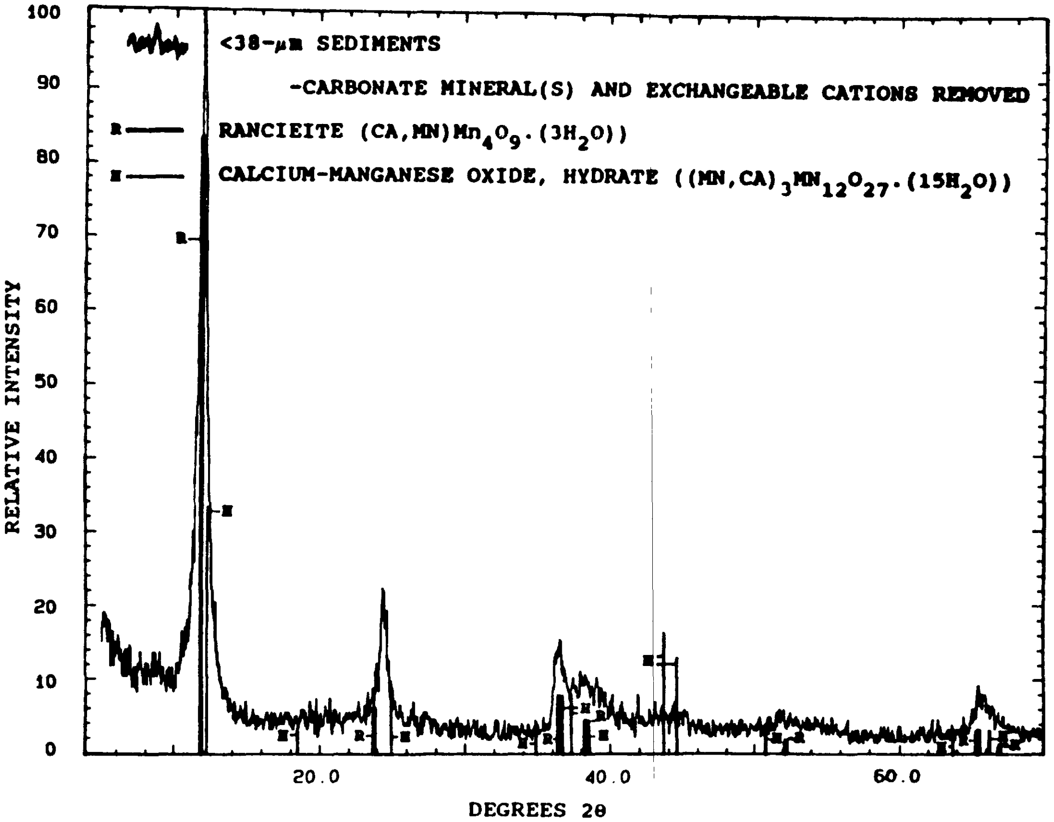

Figure 2. Graph illustrating how rancieite and hydrated multiple that contains less calcium define the manganese oxides that comprise most of the fine particulates in the black crusts.

room temperature as one of a series of metal derivatives of a metastable manganese oxyhydrate containing some sodium. The similarity of the peak locations in the XRD pattern for takanelite ($(Mn,Ca)Mn_4O_9.(3H_2O)$) (Joint Committee on Powder Diffraction Standards, pattern 25-164) to those in the pattern for rancieite adds substance to the possibility of a calcium-divalent manganese mineral series.

That some mineral(s), most likely carbonates, were removed by the ammonium acetate extraction is shown by the difference in the XRD patterns for the acetone-settled less-than-38-µm particles before and after the extraction. JCPDS patterns for most of the carbonates of calcium, magnesium, manganese, and mixtures thereof did not compare well with the patterns for the acetone-settled particles before extraction. Even for the mineral calcian kutnahorite (Joint Committee on Powder Diffraction Standards pattern 19-234) whose pattern most closely matched the sample peaks, the 100-percent-intensity peak was not indicated on the sample pattern. Kutnahorite is a calcium-manganese carbonate of variable calcium-to-manganese ratios. The form considered here has the formula $Ca_{0.74}(Mn,Mg)_{0.26}CO_3$ (fig. 3).

Nonmanganese Minerals

XRD patterns suggested that the 150- to 250-µm particles are composed primarily of quartz and plagioclase and a small amount of mica; quartz is more prominent than plagioclase on the particle surface and plagioclase is more prominent than quartz in the interior. XRD patterns of the 0.1- to 10-µm particles washed off the 150- to 250-µm fraction and of the less-than-63-µm fractions were all very similar and included the more intense peaks for mica and quartz. Mica, plagioclase, and quartz were well defined in the residues remaining after the manganese oxide removal. Peak heights, a possible indication of concentration, suggest that there is no progressive concentration change with particle size for any of these minerals. A chlorite solid was strongly evident in the XRD patterns of the less-than-38-µm particles, particularly in the 0.1- to 10-µm fraction.

The patterns for low albite (a plagioclase), clinochlore IIb (a chlorite), muscovite 3T (a mica), and low quartz (a quartz) (Joint Committee on Powder Diffraction Standards, patterns 9-466, 7-78, 7-48, and 5-490 respectively) describe the XRD patterns for the manganese-free fractions and are shown in figures 4A and 4B.

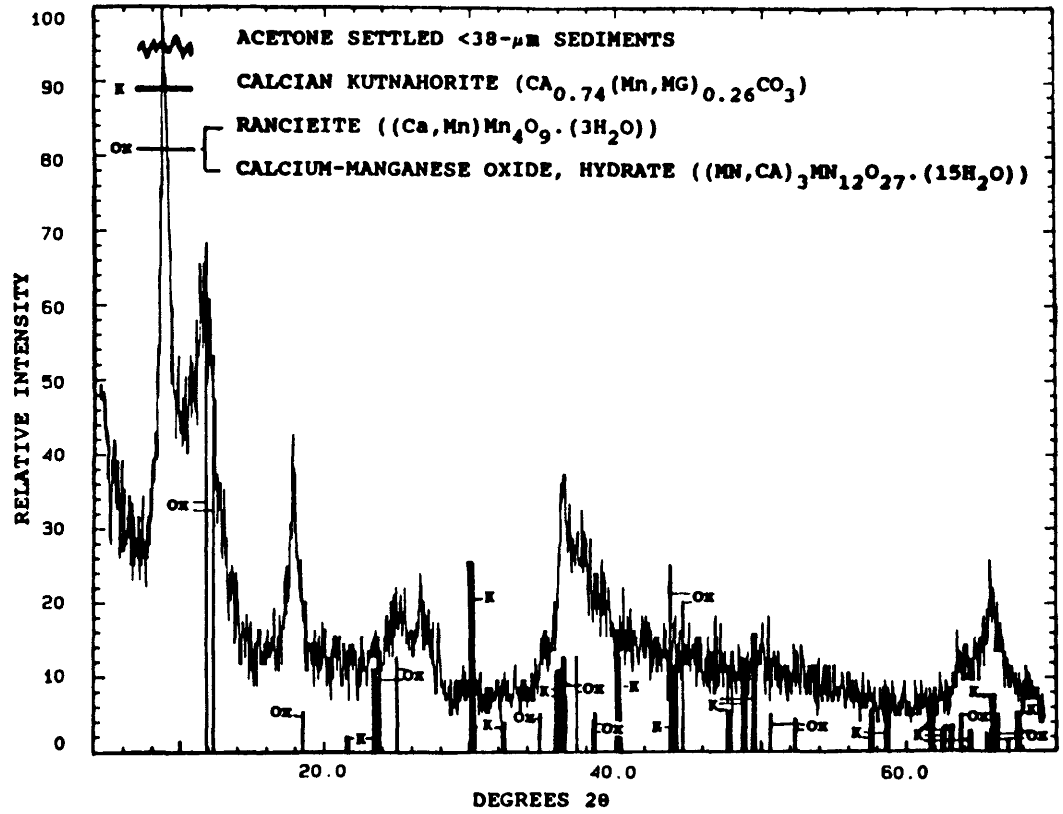

Figure 3. Graph comparing the XRD pattern for the acetone-settled solid with that of the carbonate, calcian kutnahorite. The calcium-manganese oxide patterns are also included but the patterns of the nonmanganese minerals, indicated by the high-intensity sharp peaks at low 2θ's, were excluded for graph legibility.

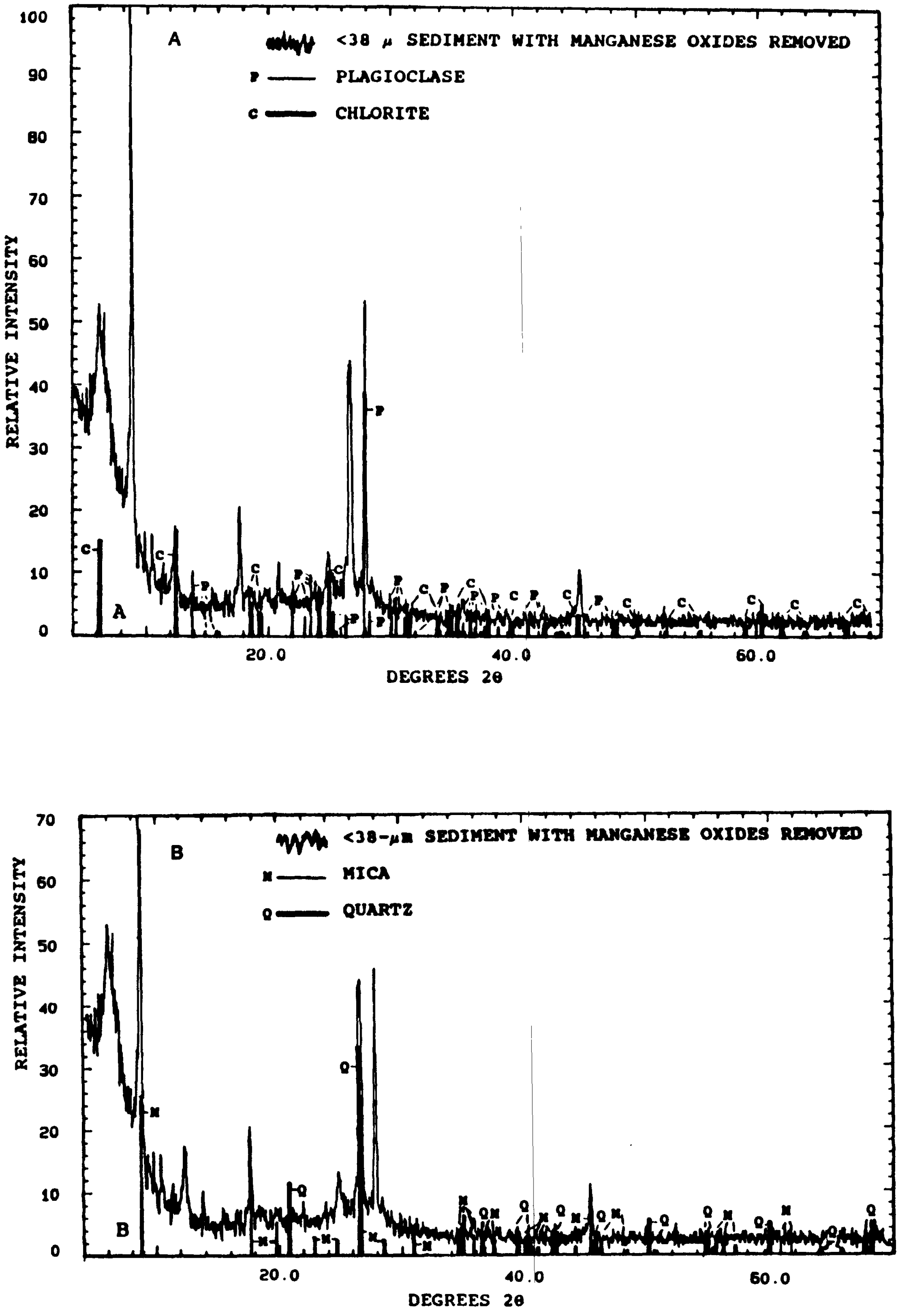

Figure 4. Graph illustrating the correlation of the sample XRD patterns with those for the nonmanganese minerals: A, chlorite and plagioclase; B, mica and quartz.

SUMMARY

Black crusts first observed in 1985 at sampling station 09498400 were separated into size fractions and the magnetic and nonmagnetic parts were segregated.

AAS analysis of leachates from sediments that had been heated in HCL at near boiling temperature indicate that iron predominates in the interior of both the magnetic and nonmagnetic 150- to 250-µm particles, but that manganese predominates over iron in the nonmagnetic fractions of the 150- to 250-µm particle surface-layers, the 0.1- to 10-µm particles washed off the 150- to 250-µm particles, and the sieved 0.1- to 10-µm particles.

The less-than-75-µm particles consist almost entirely of manganese solids. These solids have an oxidation number of 3.65 ± 0.04 and contain average cation-to-manganese molar ratios of 0.06 for iron, 0.3 for calcium, 0.03 for magnesium, and 0.045 for sodium. Chemical analysis and XRD patterns of manganese solids, free of carbonate mineral(s) and exchangeable cations, suggest a mixture of $(Ca,Mn^{2+})Mn^{4+}_4O_9$-hydrate and $(Mn^{2+},Ca)Mn^{4+}_4O_9$-hydrate. A mineral series with variable calcium-to-divalent manganese ratios, represented by takanelite and rancieite, could have manganese oxidation numbers ranging from 3.60 to 4.00. Such a mixture with domains of variable calcium-to-divalent manganese ratios may be produced in natural waters as a result of existing multiple reactions.

The carbonate mineral identity(ies) is questionable but of the probable carbonates, calcian kutnahorite ($Ca_{0.74}(Mn,Mg)_{0.26}CO_3$) best describes the undesignated peaks in XRD patterns of acetone-settled less-than-38-µm particles.

XRD patterns suggest the 150- to 250-µm particles are composed primarily of quartz and plagioclase along with a small amount of mica; quartz is more prominent than plagioclase on the particle surface and plagioclase is more prominent than quartz in the particle interior. XRD patterns of solids remaining after manganese oxide removal from the less-than-65-µm particles indicate the presence of mica, plagioclase, and quartz. A chlorite solid was strongly evident in the less-than-38-µm particles, especially in the 0.1- to 10-µm fraction. In the XRD patterns for the untreated less-than- 75-µm fractions, the manganese solids almost completely obscured the plagioclase and chlorite but not the quartz and mica.

The manganese oxides precipitate on iron-enriched large particles and as fine particulates. The iron enriched particles may derive from surface deposits that are flushed into Pinal Creek by ephemeral streams and carried downstream, from large particles that are enriched upstream and transported to the test site, and(or) from oxidation of exposed bed material at the site. The manganese oxides in the fine particulates may form as separate particles and coexist with the other identified minerals because of similar particle size. More likely, the manganese oxides form on the surfaces of one or more of the identified mineral forms, especially those of manganese carbonate, chlorite, and, possibly, plagioclase. Iron is present in all fractions and the iron-manganese oxidation cycle may have initiated the manganese oxidation. The suggested mechanisms are somewhat supported by the description of a natural deposit of takanelite; takanelite has been described as consisting of microscopic intergrowths of takanelite with goethite (α-FeOOH), manganese and aluminum silicates, and quartz in an oxidation zone of rhodochrosite ($MnCO_3$), a manganese silicate, and a manganese-magnesium silicate.

Rancieite and takanelite have been identified as mineral deposits, but this paper gives evidence of the formation of minerals of their structure in natural water. Study of the precipitation conditions may make possible the measurement of thermodynamic data for various calcium-to-divalent-manganese ratios of their mineral structures.

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MEASUREMENT OF STREAM REAERATION AT PINAL CREEK, ARIZONA

By Steve A. Longsworth[1]

ABSTRACT

A measurement of stream reaeration at Pinal Creek, Arizona, was used to determine the carbon dioxide desorption rate. In the perennial reach of Pinal Creek, degassing of carbon dioxide and ingassing of oxygen appear to control precipitation of manganese oxides, which affects the movement and mobility of other metal compounds. After preliminary field work in January and March 1990, rhodamine WT[2] *dye and propane tracers were injected and sampled in a 2.1-kilometer reach in December 1990. Stream velocities in December were 73 to 181 percent greater than the velocities measured in March, even though discharge was 7 to 24 percent less. Less than 25 percent of the injected dye was recovered. The measured propane desorption coefficient was 1.63 per hour at 15.0 degrees Celsius for the 1.0-kilometer reach between sampling points. At 20.0 degrees Celsius, the rate coefficients were 1.84 per hour for propane, 2.55 per hour for oxygen, and 2.28 per hour for carbon dioxide. The values are uncertain because of the limited available reach length and traveltime, and the small amount of dye recovered.*

INTRODUCTION

The measurement of reaeration by use of tracers and the subsequent determination of carbon dioxide (CO_2) desorption rate could aid in understanding factors controlling transport and precipitation of metal compounds in Pinal Creek, near Globe, Ariz. Degassing of CO_2 and ingassing of oxygen (O_2) appear to control precipitation of manganese (Mn) oxides in a 6-km (kilometer) perennial-flow reach where pH increased 1.5 units, dissolved Mn decreased 80 percent, and dissolved inorganic carbon decreased 45 percent in March 1990 (Eychaner, 1991, this Proceedings). This paper presents the results of a reaeration study where measurements of O_2 absorption and associated CO_2 desorption rates were made in December 1990 at Pinal Creek.

Stream reaeration is the physical absorption of O_2 from the atmosphere by a flowing stream. Gas exchange between the atmosphere and a stream is a first-order process (Bennett and Rathbun, 1972) and is shown as

$$\frac{dC}{dt} = -K(C-C_S), \qquad (1)$$

where

$\frac{dC}{dt}$ = the rate of change of gas concentration, in milligrams per liter per hour,
K = a rate constant, in inverse hours (1 hour),
C = the dissolved-gas concentration at time t, in milligrams per liter, and
C_S = the saturation concentration in equilibrium with the atmosphere, in milligrams per liter.

The value of K depends primarily on the surface area of the stream reach under consideration and the temperature and turbulence of the stream. For two gases, *a* and *b*, the ratio K_a/K_b is constant, independent of temperature or turbulence intensity (Tsivoglou, 1967). Measurement of the desorption coefficient (K_p) for the tracer gas propane, therefore, allows computation of the reaeration coefficient by

$$K_{O_2} = (1.39)K_p \qquad (2)$$

(Kilpatrick and others, 1989) and the CO_2 desorption coefficient by (Tsivoglou, 1967).

$$K_{CO_2} = (0.894)K_{O_2} \qquad (3)$$

Field reaeration measurements involve slug injection of a dye tracer at the beginning of a continuous injection of propane gas; water samples are collected at two or more downstream points (Kilpatrick and others, 1989). Complete passage of the dye cloud at a sample point indicates that propane concentration has reached a plateau and propane samples can be collected. A computer program written by D.L. Stedfast (U.S. Geological Survey, written commun., 1990) was used to compute the desorption coefficient from dye-concentration hydrographs, plateau propane concentrations, and discharges measured at the sample points. Rate coefficients commonly are presented for a standard stream temperature of 20 °C (degrees Celsius). Field measurements can be adjusted to 20 °C by

$$K_{20} = 1.0241^{(20-T)}K_T \qquad (4)$$

(Kilpatrick and others, 1989), where K_T is a rate coefficient measured at temperature, T.

Field-reaeration measurements are accurate only for the stream conditions at the time of measurement. Reaeration rates are affected by climate factors such as windspeed, humidity, and temperature; general channel features such as slope, width, depth, and roughness; biological activity such as photosynthesis and plant respiration; and stream chemistry (Bennett and Rathbun, 1972; Kilpatrick and others, 1989).

Perennial flow in Pinal Creek begins about 6 km upstream from streamflow-gaging station 09498400, Pinal Creek at Inspiration Dam (fig. 1). The stream channel generally meanders but includes braided segments. Inspiration Dam marks a sharp break in channel slope; upstream from Inspiration Dam, slope averages 9 m/km (meters per kilometer) and in the narrow canyon downstream, average channel slope increases to 26 m/km. Upstream from Inspiration Dam, stream width ranges from 1.5 to 3.5 m (meters) and depth ranges

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[1] U.S. Geological Survey, Tucson, Ariz.

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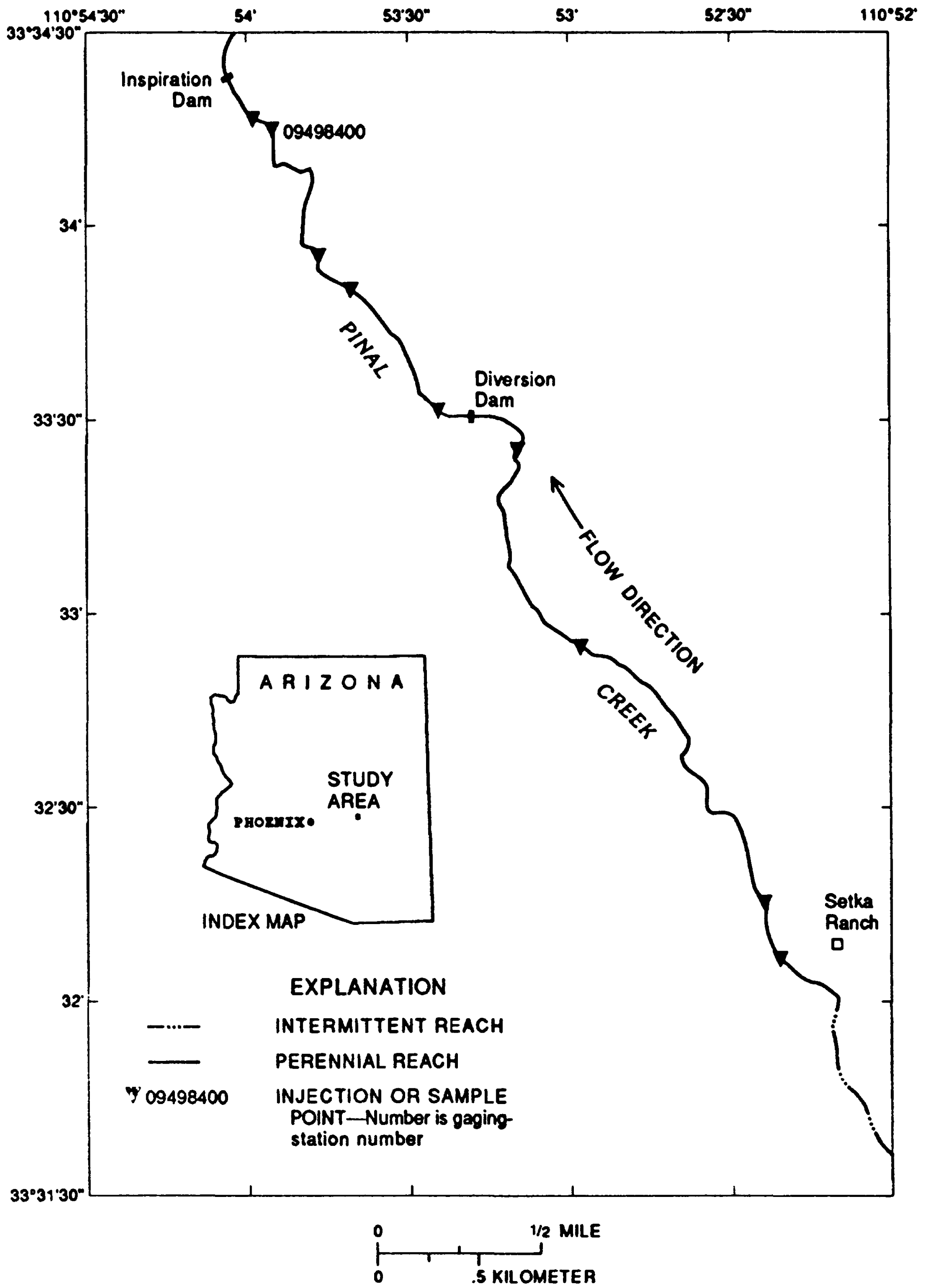
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33°31'30"
Inspiration Dam
09498400
PINAL
Diversion Dam
FLOW DIRECTION
CREEK
Setka Ranch
ARIZONA
STUDY AREA
PHOENIX
INDEX MAP
EXPLANATION
INTERMITTENT REACH
PERENNIAL REACH
09498400 INJECTION OR SAMPLE POINT—Number is gaging-station number
0
1/2 MILE
0
.5 KILOMETER

Figure 1. Location of study area and sample sites.

from about 0.1 to 0.3 m in small pools. This reach of Pinal Creek, however, is further divided about 2.5 km upstream from Inspiration Dam by an earthen diversion dam and pond (fig. 2). The pond contains about 9 hours of streamflow at a discharge of 0.2 m^3/s (cubic meters per second).

Sample points along Pinal Creek were selected on the basis of mixing length and stream morphology. The upstream sample location should allow 1 hour traveltime from the injection point to ensure that the propane is fully dissolved (Kilpatrick and others, 1989). The second sample point should allow the product of the estimated propane desorption coefficient and the traveltime between sample points to exceed 1 (Kilpatrick and others, 1989). These requirements were constrained, however, by the morphology of Pinal Creek. Because the channel-slope change and diversion dam affected streamflow, the perennial reach above Inspiration Dam was divided into two test sections: an upper reach from near the head of flow to 300 m above the diversion dam and a lower reach from below the diversion dam to about 250 m above Inspiration Dam (fig. 2).

PRELIMINARY WORK

General flow and channel conditions were determined during January 1990. A solution containing 0.0029 kilogram of rhodamine WT dye was slug injected near the point where perennial flow begins, and traveltimes to four sample points were measured (fig. 2). Stream velocity averaged 1.5 km/hr (kilometers per hour) above the diversion dam and 0.9 km/hr below the dam (table 1).

A reaeration measurement was attempted with limited success in March 1990. Two test reaches were used to avoid effects of the diversion dam on streamflow (fig. 2). In coordination with other streamflow-chemistry studies (Eychaner, 1991, this Proceedings), dye and propane were injected at points above and below the diversion dam, and samples were collected from two points in each reach (table 1). Average velocities were 0.95 km/hr above the diversion dam and 0.82 km/hr below the diversion dam. Unfortunately, propane was not detected in water from three of the four sampling points, and therefore, reaeration coefficients could not be computed. The failure to detect propane was thought to be caused by the use of inefficient diffusers resulting in insufficient initial propane concentrations.

REAERATION MEASUREMENT

Sample points for the followup study in December 1990 were selected for reaches upstream and downstream from the diversion dam based on stream velocities and traveltimes measured in the preliminary work. However, equipment problems in the field prevented measurements in the reach upstream from the diversion dam and so only one set of measurements was obtained.

In the reach below the diversion dam, sample points were located 1,064 m and 2,099 m downstream from the injection point. The first site was located an estimated 1 hour traveltime from the injection point and the second site was located where the product of the desorption coefficient and peak-dye concentration traveltime was estimated to be 0.98. The calculated stream length required for adequate lateral mixing of tracers was 238 m and samples were obtained from the center of flow. To increase initial propane concentrations, more efficient diffusers were used and five of these were installed in an artificial pool at an average submergence of 0.25 m to increase contact time.

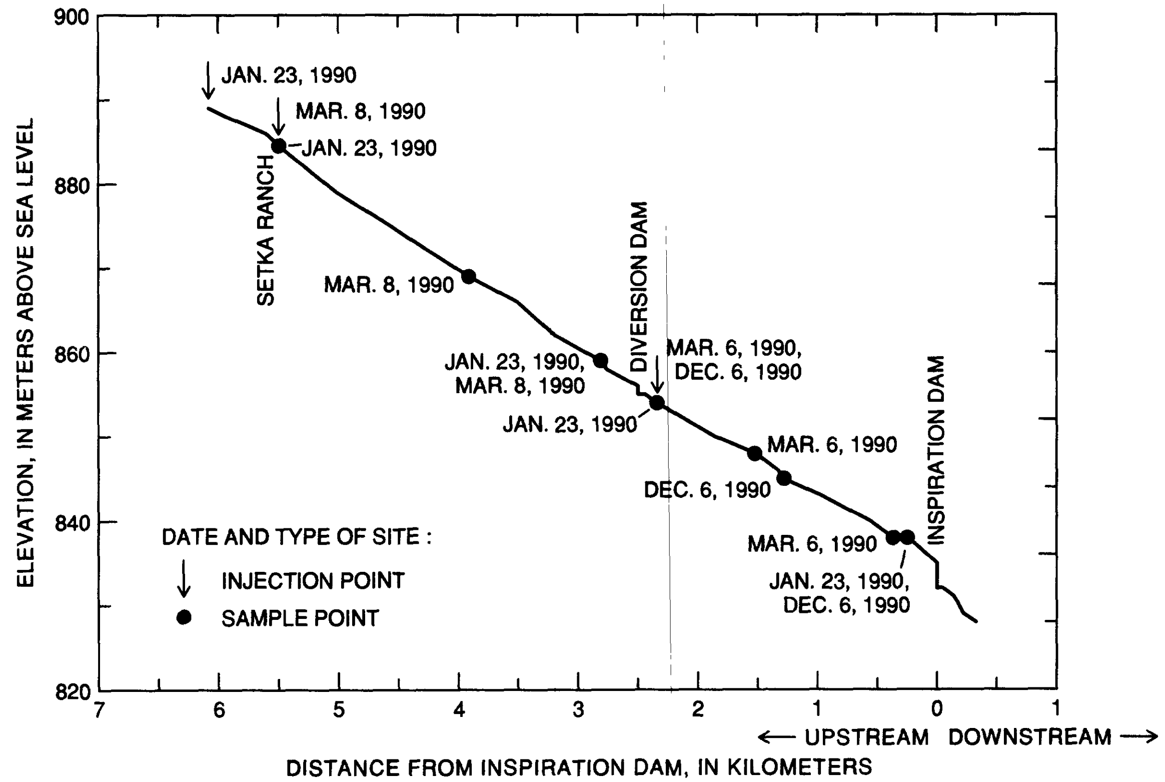

Figure 2. Profile of selected perennial reach of Pinal Creek and study locations.

Table 1. *Traveltime data for Pinal Creek, January and March 1990*

[m^3/s, cubic meters per second; km/hr, kilometers per hour; dashes indicate no data]

			Peak dye concentration	
Date	Distance from injection point (meters)	Discharge (m^3/s)	Cumulative time of travel (minutes)	Subreach velocity (km/hr)
		Above diversion dam		
1-23-90	475	--	18	1.6
1-23-90	3,266	--	120	1.4
3-8-90	1,698	0.164	74	1.4
3-8-90	2,791	.204	[1]132	.50
		Below diversion dam		
1-23-90	[2]1,977	--	139	.86
3-6-90	0	.134	0	--
3-6-90	820	.133	46	1.1
3-6-90	1,977	.170	[1]132	.53

[1] Estimated.

[2] Distance between sample points.

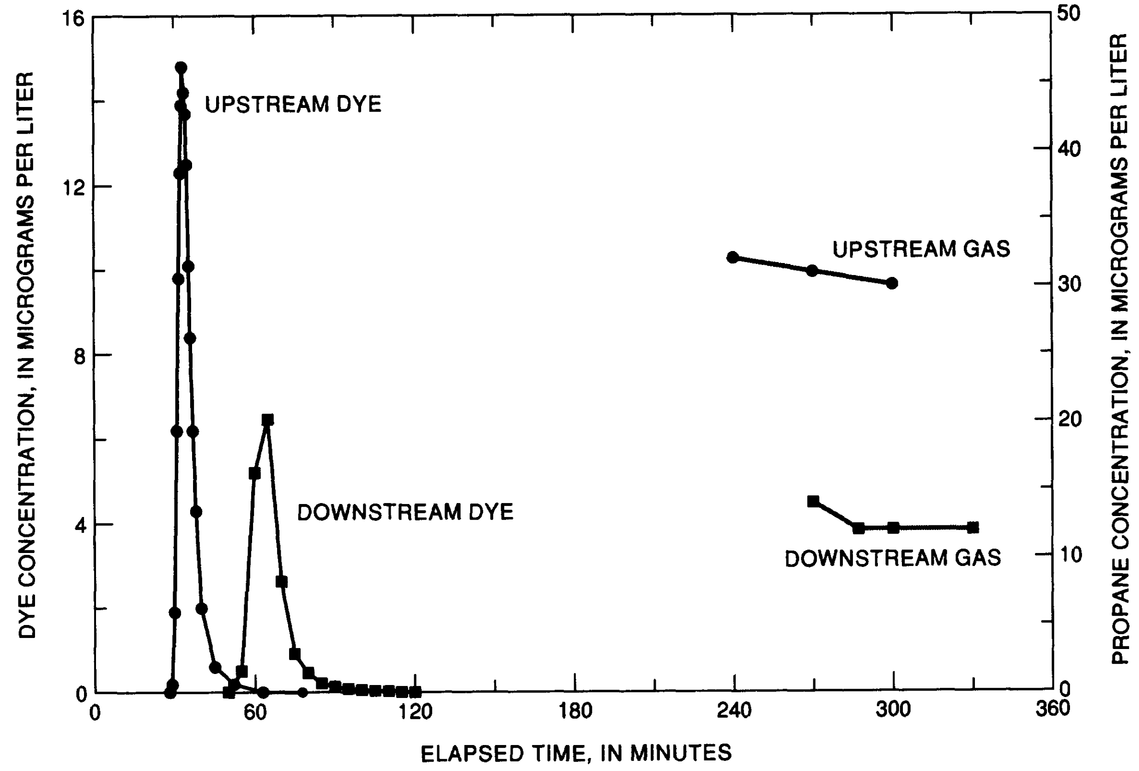

Figure 3. Dye and propane data for Pinal Creek, December 6, 1990.

Current-meter discharge measurements were made twice at the injection point and at each of the two sampling points. Propane samples were collected after the dye cloud passed each sampling point as detected by field fluorometry (fig. 3).

Propane concentrations varied by 2 micrograms per liter in the three samples from the upstream sampling point and in four samples from the downstream sampling point (table 2). However, concentrations in three of the four samples from the downstream sampling point were equal. The propane desorption coefficient calculated using the average propane concentrations (table 2) was 1.57 per hour at the field temperature of 15.0 °C. Rate coefficients for standard conditions at 20.0 °C were 1.77 per hour for

Table 2. *Reaeration data from December 1990 study, Pinal Creek*

[m^3/s, cubic meters per second; km/hr, kilometers per hour; µg/L, micrograms per liter; dashes indicate no data]

			Peak dye concentration		Propane	
Date	Distance from injection point (meters)	Discharge (m^3/s)	Cumulative time of travel (minutes)	Subreach velocity (km/hr)	Concentration (µg/L)	Elapsed time from injection (minutes)
12-6-90	0	0.125	0	--	--	--
12-6-90	1,064 upstream	.116	33	1.9	32	240
					31	270
					30	300
					Average 31	
12-6-90	2,099 downstream	.130	65	.96	14	270
					12	287
					12	300
					12	330
					Average 12.5	

propane, 2.46 per hour for oxygen, and 2.20 per hour for carbon dioxide. Although these rates are influenced by several factors, the calculated oxygen transfer rate, or reaeration coefficient, is consistent with measured coefficients for streams of comparable size and geometry as discussed in Bennett and Rathbun (1972). A propane desorption coefficient of 1.77 per hour was also obtained by use of an empirical equation (Kilpatrick and others, 1989) on the basis of measured traveltimes and channel slope.

DISCUSSION

Although the entire available reach was used for the reaeration study, traveltimes were less than recommended by Kilpatrick and others (1989). The 33-minute traveltime to the first sample point could have caused an overestimate of the propane desorption coefficient if propane sampled at the first sampling point was not completely in solution. Subreach velocity in December was at least 70 percent greater than in March although discharge measured in December was 7 to 24 percent less than in March (table 2). The stream reach below the diversion dam was scoured when a flood peak of about 55 m^3/s washed out the diversion dam in July 1990; the dam was replaced in November 1990. The variablity in propane concentration at the upstream sampling point also may indicate that part of the propane was not in complete solution with streamwater.

Only 23.1 percent of the dye was recovered at the upstream sample point and 21.8 percent at the downstream sampling point. The large dye loss could have been caused by shallow ground-water pumping near the channel in the first 400 m. Large dye losses related to algae, suspended sediment, or instream chemical reactions were unlikely because of the small dye loss in the lower subreach, the short traveltimes, and the small algal population. Interchange of streamflow with water in coarse substream sediments (Bencala and others, 1984) could also cause dye loss. The fact that most loss occurred in the upper subreach supports the idea of losses to ground-water pumping. Because the dye cloud arrived at the downstream sampling point less than 5 minutes before the first sample was collected, a background dye sample was not collected. An estimated arrival time of the leading edge of the dye cloud was used in calculating dye loss and gas-transfer rates.

CONCLUSIONS

The reaeration rate measured at Pinal Creek represents streamflow conditions below the diversion dam during field work in December 1990. Stream conditions on the upper reach of Pinal Creek are similar to conditions in the lower reach except that no streamflow is diverted and algal populations appear to be more abundant. Significant changes in streamflow conditions have been observed within a 1-year period. The gas-transfer rates measured will vary because of changes in climatic conditions, channel geometry, ground-water pumping rates, and longitudinal variations in stream chemistry. Photosynthesis and plant respiration also affect gas-transfer rates; therefore, seasonal variations of algal populations could be important.

Use of the CO2 desorption coefficient to measure carbon dioxide flux from Pinal Creek would require calculation of CO2 partial pressures from pH and alkalinity measurements using a geochemical model. The computed gas-exchange rates, however, could be in error. Short traveltimes may have resulted in computed rates of gas exchange greater than actual rates. The calculated rates are consistent with rates from streams of similar size, but additional measurements may be required to reduce the uncertainty of error. More information on the interchange of shallow ground water and streamflow is needed to determine the effects on gas-transfer rates.

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APPLICATION OF MINTEQA2 TO THE SPECIATION OF CONTAMINANTS AT GLOBE, ARIZONA

By Kevin J. Novo-Gradac[1] *and* Charles N. Smith[2]

ABSTRACT

The geochemical speciation model MINTEQA2 was applied to study the movement of highly acidic contaminants through a carbonate-bearing aquifer underlying a mine waste site at Globe, Arizona. The MINTEQA2 code was modified to allow the aquifer to be represented as a column through which a finite amount of contaminated water was allowed to pass. The distribution of contaminants among dissolved, adsorbed, and precipitated phases was tracked as a function of distance and the volume of acidic water that passed through the column. This type of modeling allows for an estimation of total contaminant loading within the column and forecasting of breakthrough events. This approach and its computer code may have further applications in the evaluation of in-situ remediation options.

INTRODUCTION

Highly acidic water resulting from the oxidation of sulfide-bearing copper ores and gangue have contaminated an aquifer near Globe, Ariz. Calcite dissolution has been identified as the major process retarding the movement of the acidic water and also imposes a solubility control for many of the related contaminants (Eychaner and Stollenwerk, 1985). At the site, a plume of acidic water extends 15 km (kilometers) from the source through alluvium and the Gila Conglomerate. Both of these materials are now devoid of calcite in this zone. In a relatively short interval (2 km), the pH rises rapidly from approximately 4 to 6.1. Alluvium in this region was determined to contain 0.34-percent calcite (by weight) and the Gila Conglomerate contains 1.25-percent calcite (by weight). Modeling of the processes controlling the dissolution of calcite and the sorption or precipitation of contaminants provides important information for establishing control of the pollutants.

The chemical behavior of these highly acidic waters as they pass through calcite-containing bedrock was approximated by a "column"-type speciation-modeling approach. MINTEQA2 was modified to keep track of the dissolved, adsorbed, and precipitated amounts of each component after speciation (Allison and others, 1991).

In the model simulation, the contaminated solution is placed in the first of a series of cells and allowed to equilibrate with the solid phase present in that cell. The solute from this first cell is then passed into the second cell where it reacts with the solids present in that cell. This process is repeated for a finite number of cells. This process provides a representation of a column in MINTEQA2.

When another contaminant pulse is added to the column, the pollutant reacts with the solids that remained there after the previous pulse. This process is then repeated for a finite number of pulses (pore volumes of contaminant). This column modeling approach provides a pseudo-transport coupled code that potentially allows for the incorporation of many powerful features. This part of the MINTEQA2 code is in an early stage of development however, and is difficult to use in its current state. Currently, the model only allows for an initially homogenous sediment column and an infinite source.

PROCEDURE

The sediments at the site were assumed to be homogeneous and to initially contain 0.34-percent calcite (by weight). This value represents the lower of the two values for calcite content in typical Globe sediments. Additional properties of the sediments were estimated: porosity, 50-percent; density of sediment, 2.6 gram per cubic centimeter. A diffuse-layer methodology that incorporated the equilibrium constants from Dzombak (1986) was used to model sorption. The sediments were assumed to contain a fixed amount of an iron oxyhydroxide adsorbent phase (estimated to be 10.0 grams per liter of solution) (Loux and others, 1989). Otherwise, the sediments were assumed to be inert in this modeling exercise.

The chemical characteristics for the contaminated water were obtained from Eychaner and Stollenwerk (1985) and are shown in table 1. In addition to these data, the P_{CO2} was set to 0.01 atmosphere. This value is somewhat higher than the normal partial pressure for air and somewhat lower than that found in many sediments.

Table 1. *Component concentrations used as input to MINTEQA2*

[Values from Eychaner and Stollenwerk, 1985]

Element	Concentration (millimolal)
Ca	12.4
Mg	16.1
Na	10.1
K	.242
Cl	11.3
S	114.
Fe	54.4
Mn	1.35
Al	11.4
Cd	.0037
Cu	2.42
Ni	.066
Zn	.291

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[1] AScI Corporation, Athens, Ga.

[2] U.S. Environmental Protection Agency, Environmental Research Laboratory, Athens, Ga.

A 50-cell by 80-pulse (4,000 step) column-type run, to represent the leaching by 80 pore volumes of contaminant, was performed with the Globe data. In this run, adsorption and precipitation were allowed but no oxidation/reduction reactions were permitted. The pH was allowed to change in response to the dissolution of calcite and the adsorption or precipitation of other constituents. To allow pH to vary, an initial MINTEQA2 run was performed to calculate the total H^+ concentration for input to the column-style runs. In this run, the pH was fixed at 3.6 (Eychaner and Stollenwerk, 1985) and no solids were allowed to precipitate. The total component concentrations from this run then constituted the initial input to cell one of the column.

ANALYSIS

This study demonstrates the effect of calcite dissolution and adsorption on the transport of contaminants when oxidation/reduction processes are not allowed to occur. Under these conditions, a number of interesting observations about the column become apparent.

A plot of the pH (fig. 1) in each cell at time (t) = 80 (when the 80th pulse has just equilibrated in the first cell) reveals that the pH changes in a very stepwise fashion within the column. This result is not very consistent with the data obtained at the site. Sediments at the site contain a low-pH zone that is relatively constant until the very front of the plume where the pH rises rapidly over a very small (2-km) interval.

When the plot of pH (fig. 1) is compared with the plot for Fe^{2+} at t = 80 (fig. 2), it becomes apparent that the solubility of Fe^{2+} and the pH of solution are strongly correlated to each other. This is not surprising because the solubility of $FeCO_3$ depends on the CO_3^{2-} anion concentration.

Cd speciation likewise is very dependent on the pH and the concentration of CO_3^{2-} and provides an illustration of how metals can be greatly concentrated in certain zones within the aquifer. The concentration of dissolved, adsorbed, and precipitated Cd in the column at three different times (t = 20, 50, and 80) is shown in figure 3a-c. Cd initially adsorbs to the iron oxyhydroxide adsorbent surface. Eventually, Cd also precipitates in the form of otavite as it moves through the column. The bulk of the Cd backs up in response to the pH gradient in the column and progresses in response to the movement of this gradient.

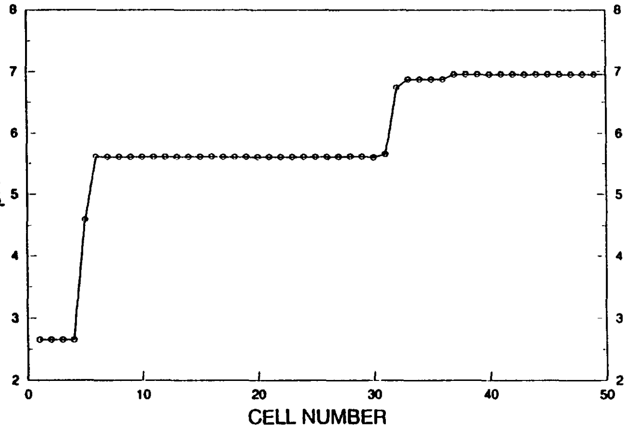

Figure 1. Predicted pH distribution in the column after 80 pore volumes of contaminated water.

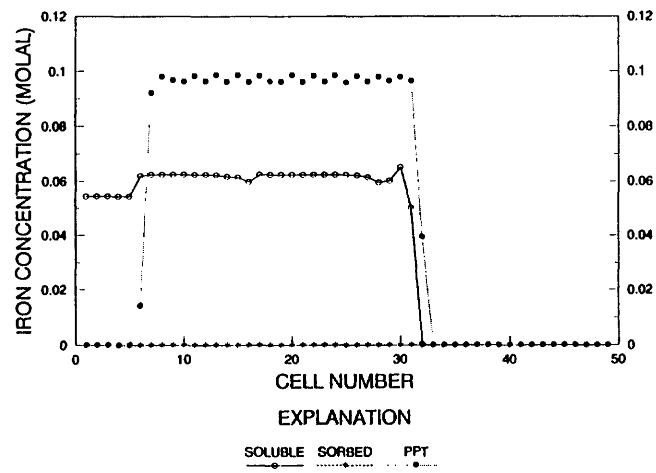

Figure 2. The spatial distribution of Fe(II) among dissolved, adsorbed, and precipitated fractions in the model column after addition of 80 pore volumes of contaminated water.

As shown in figure 4a-c, metals can exhibit diverse speciation behavior, and the arrival times of metal contaminants are shown to differ substantially. A Mn^{2+} front would be expected to arrive early compared to those of Cu^{2+} or Al^{3+}, which the model predicts would arrive with waters that have a lower pH. This behavior reflects the variability in the solubility behavior of these metals as a function of pH.

The results of this study lead to a logical second step that includes the oxidation of Fe(II) to Fe(III). When oxidation of Fe(II) to Fe(III) is allowed to occur in these solutions, $Fe(OH)_3$ related precipitates are predicted. If this process occurred, two equivalents of H^+ would form for every Fe^{2+} undergoing the oxidation and precipitation. The problem with incorporating this redox expression is that the rate of oxidation is very slow and a kinetic expression involving pH and Fe^{2+} concentration will have to be incorporated into an otherwise equilibrium-based code. Work will continue in this area to correct this obvious shortcoming of the first modeling sequence described above.

CONCLUSIONS

A metal-speciation model that incorporates even a crude emulation of transport processes can provide valuable insight into the accumulation of mass, time of arrival, and leaching times of contaminants. The modeled concentrations of dissolved constituents as a function of pH do not correlate very well with actual data collected at the site; however, the model results exhibit trends that are similar to those observed at the site. It is likely that most of the differences between model predictions and observed data can be accounted for by the absence of Fe^{2+}/Fe^{3+} redox kinetics in this model. It also is likely that a coupling to a transport model, rather than the simple column arrangement, will improve model predictions.

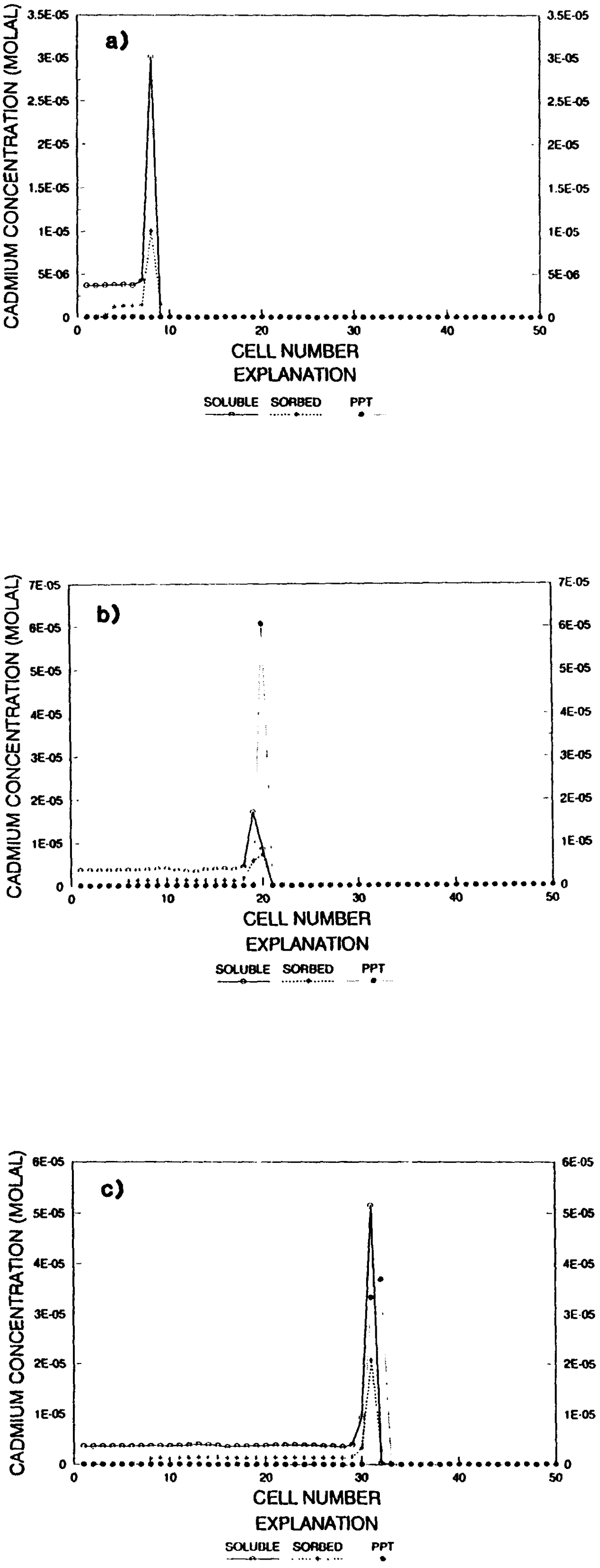

Figure 3. The spatial distribution of Cd among dissolved, adsorbed, and precipitated fractions in the column after addition of (a) 20 pore volumes, (b) 50 pore volumes, and (c) 80 pore volumes of contaminant.

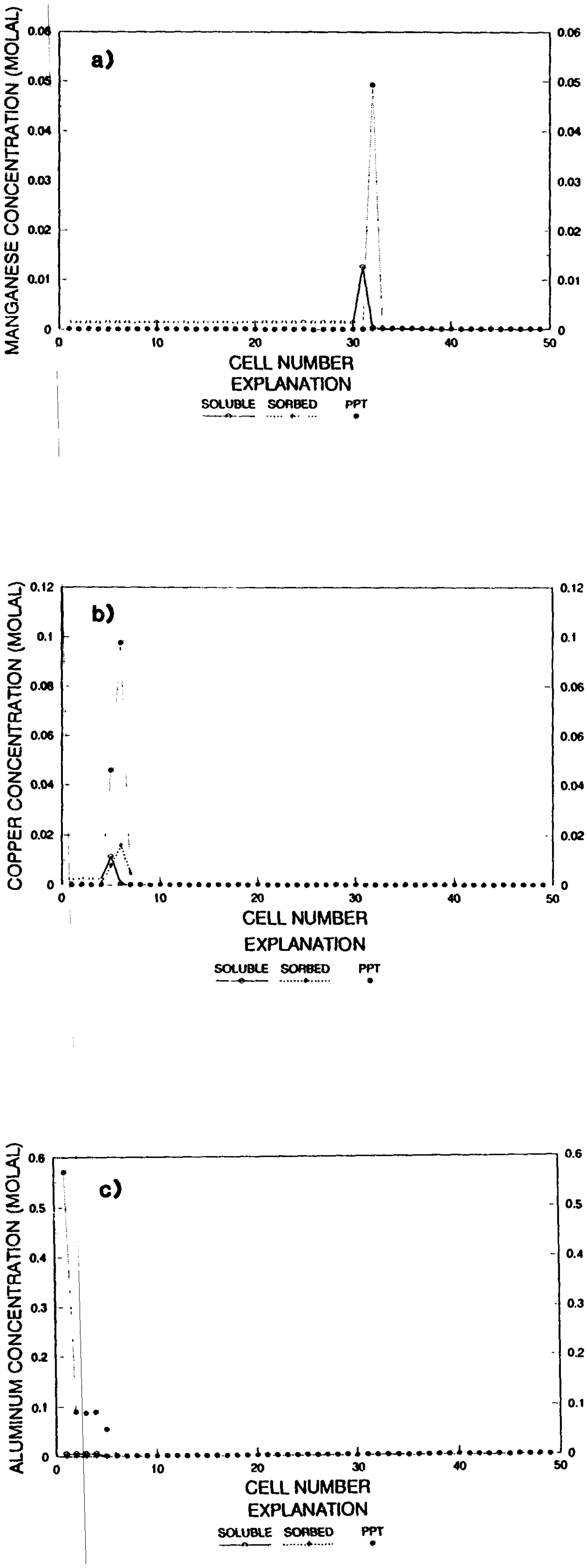

Figure 4. The spatial distribution of (a) Mn, (b) Cu, and (c) Al after 80 pore volumes of contaminant have passed cell one.

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SIMULATION OF COPPER, COBALT, AND NICKEL SORPTION IN AN ALLUVIAL AQUIFER NEAR GLOBE, ARIZONA

By Kenneth G. Stollenwerk[1]

ABSTRACT

Acidic water with elevated concentrations of metals has contaminated an alluvial aquifer near Globe, Arizona. Reactions between alluvium and acidic ground water were first evaluated in laboratory column experiments. The geochemical equilibrium speciation model MINTEQA2 was then used to simulate the observed changes in concentration of aqueous constituents in the column breakthrough curves. Attenuation of copper, cobalt, and nickel in the column experiments was a function of pH and could be quantitatively modeled by the diffuse-layer surface-complexation model in MINTEQA2. Intrinsic equilibrium constants for sorption of copper and nickel on ferrihydrite were obtained from a compilation of published sorption constants: for copper, $LogK^{int} = 0.6$; *for nickel,* $LogK^{int} = -2.5$. *The intrinsic equilibrium constant for cobalt was fit to the column experimental data;* $LogK^{int} = -2.0$.

The geochemical model was then used to simulate the observed changes in concentration of aqueous constituents along a flow path in the aquifer. Attenuation of copper, cobalt, and nickel along the flow path was simulated reasonably well using the diffuse layer model and the same intrinsic equilibrium constants used to simulate the column data.

INTRODUCTION

Seepage of acidic mining and milling process solutions has resulted in a plume of acidic ground water in parts of the Pinal Creek drainage basin (fig. 1). The most likely source of contamination is the acidic lake in Webster Gulch and perhaps smaller acidic ponds in the area (Envirologic Systems, Inc., 1983). Ground water in Miami Wash, the most contaminated zone, is characterized by low pH and large concentrations of dissolved metals and sulfate (table 1). Reducing conditions in the acidic ground water are evident from the presence of ferrous iron [Fe(II)] and low concentrations of dissolved oxygen (O_2). Concentrations of dissolved constituents in the acidic ground water are attenuated along the flow path by dilution with ground water from other sources and through chemical reactions. Most constituents have been attenuated along the flow path; only the more soluble constituents including calcium (Ca), sulfate (SO_4), and manganese (Mn), have increased in concentration at the streamflow gaging station (fig. 1, table 1). Hydrologic and geochemical aspects of the study area have been discussed by Eychaner (1989) and Stollenwerk and Eychaner (1989).

Prediction of future plume migration and development of remediation strategies for this aquifer will require a quantitative description of the mechanisms responsible for the current distribution of constituents in ground water. Results from laboratory column experiments were used in conjunction with data from observation wells to develop a conceptual geochemical model of the aquifer. Breakthrough curves for sixteen chemical constituents from the column experiments were simulated using the geochemical computer code MINTEQA2 (Allison and others, 1991), and thermodynamic equilibrium constants were adjusted as necessary to match experimental data. Then, the geochemical model was tested in simulations of the observed changes in concentration of constituents along a flow path in the aquifer. This paper describes results of model simulations of copper (Cu), cobalt (Co), and nickel (Ni).

METHODS

Experimental

A plexiglass column 80 cm (centimeters) long with a 5-cm inside diameter was packed with the <2 millimeter fraction of alluvium collected from an abandoned gravel quarry located adjacent to Pinal Creek, upstream from the confluence with Miami Wash. The alluvium has not been contaminated by the acidic plume; it is composed of fragments of igneous rocks and limestone from the nearby highlands and contains approximately 0.3 percent carbonate (Peterson, 1962). Acidic ground water from site 50 in Miami Wash and ground water from site 2, uncontaminated by the acidic plume were used in laboratory experiments (fig. 2). Both were filtered in the field through a 0.4 µm (micrometer) filter into Pyrex[2] bottles and stored in the dark at 4°C (degrees Celsius) until needed. Ground-water compositions are listed in table 1. Several pore volumes of uncontaminated ground water were eluted through the alluvium to rinse off soluble salts and establish a precontamintion baseline. Acidic ground water was then eluted through the alluvium until the effluent concentration of all constituents listed in table 1 was equal to the influent concentration. Direction of flow was from the bottom of the column to the top. The entire experimental setup was contained in a Plexiglas glove box under a nitrogen atmosphere to prevent atmospheric oxidation of Fe(II). An inline 0.4 µm filter was used to remove particulates from the effluent prior to sample collection by an automated fraction collector. Specific conductance and pH were measured in the glove box. Samples were then acidified and removed for analysis. Cu, Co, and Ni, were determined with a Jarrell-Ash Atom Comp 975 inductively coupled plasma atomic emission spectrophotometer.

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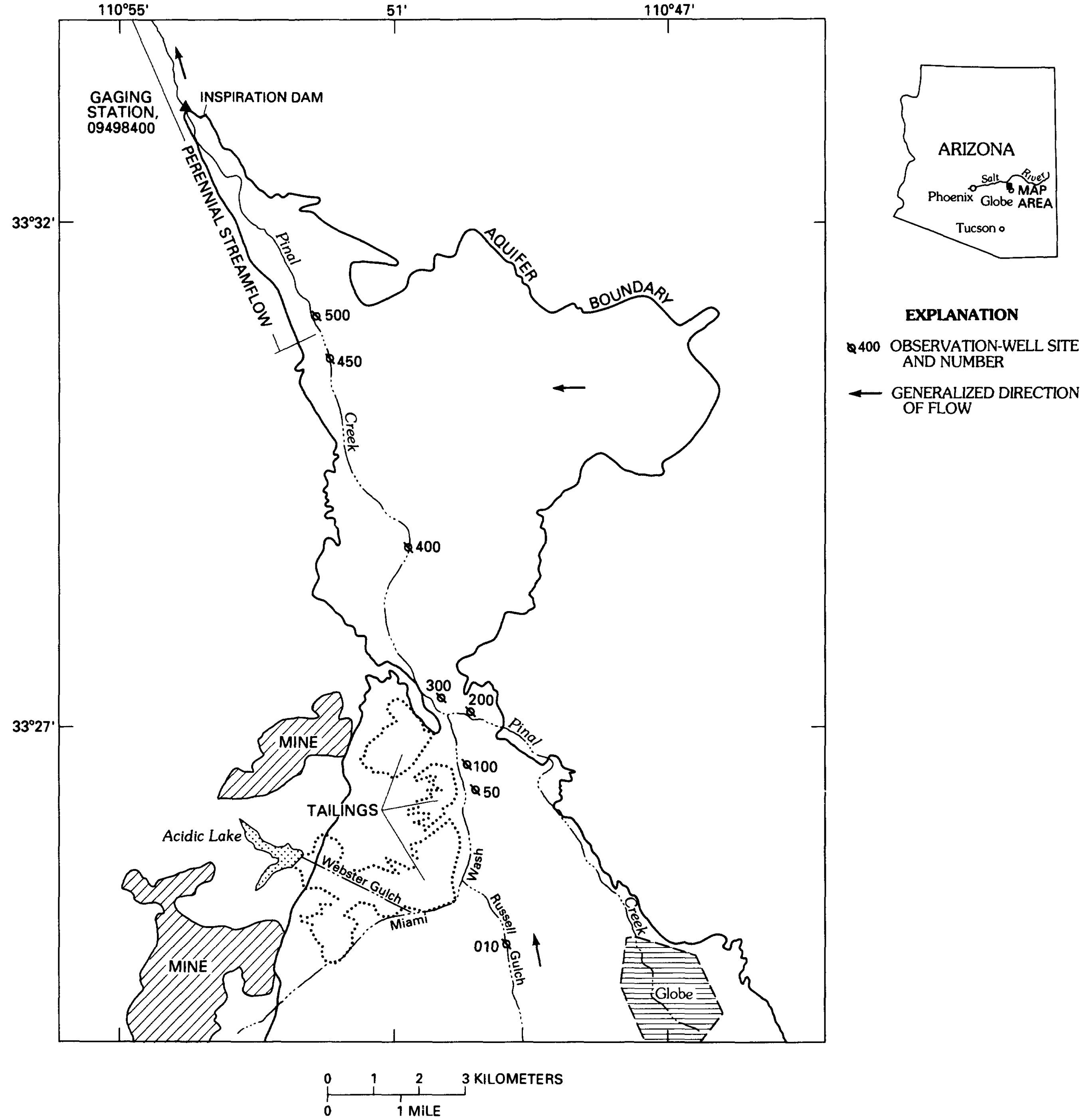
[1] U.S. Geological Survey, Denver, Colo.

[2] Use of brand, firm, or trade names in this paper is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.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GAGING STATION, 09498400
INSPIRATION DAM
PERENNIAL STREAMFLOW
Pinal
AQUIFER
BOUNDARY
500
450
Creek
400
300
200
Pinal
100
50
MINE
TAILINGS
Acidic Lake
Webster Gulch
Miami
Wash
Russell Gulch
010
Creek
Globe
MINE
ARIZONA
Salt River
Phoenix
Globe
MAP AREA
Tucson
EXPLANATION
400 OBSERVATION-WELL SITE AND NUMBER
GENERALIZED DIRECTION OF FLOW
0 1 2 3 KILOMETERS
0 1 MILE

Figure 1. Area of study. (Modified from Eychaner, 1989, fig. J-1.)

Model simulations

Reactions between acidic ground water and alluvium were simulated with MINTEQA2. Thermodynamic constants for solid and aqueous phases of Co, obtained from Naumov and others (1971), were added to the MINTEQA2 data base. Results of simulations indicate that all water samples from observation wells and laboratory experiments were undersaturated with respect to Cu, Co, and Ni minerals. Therefore, sorption by metal oxides was presumed to be the most likely attenuation mechanism for these metals. The diffuse-layer surface-complexation model option in MINTEQA2 was used to simulate sorption reactions. Data required for the diffuse-layer model include the surface area and sorption site concentration for a particular metal oxide, and the equilibrium constants that describe the sorption reactions. The most abundant metal oxides on alluvium from the gravel quarry were ferrihydrite ($Fe(OH)_3$) and manganese dioxide (MnO_2). Also, the zone of most active sorption of Co, Cu, and Ni in both the aquifer and column experiments coincided with oxidation of Fe(II) and precipitation of $Fe(OH)_3$; therefore, $Fe(OH)_3$ was used as the sorbent in model simulations. In the O_2-depleted atmosphere of the laboratory glove box, Fe(II) was oxidized by the Mn(IV) in MnO_2, whereas a combination of MnO_2 and O_2 oxidized Fe(II) in the aquifer.

Table 1. *Initial and final water composition along simulated flow path*

[mmol/L, millimoles per liter; <, less than analytical detection]

	Aqueous concentration (mmol/L)		
Constituent	Miami Wash-site 50[1]	Gaging Station	Uncontaminated[1,2]
Fe(II)	52	<	<
Ca	12	14	1.2
Mg	16	4.9	.37
Na	9.6	3.3	0.96
Al	10	<	<
Mn	1.3	0.45	<
Co	0.2	<	<
Cu	2.5	<	<
Ni	.06	<	<
Zn	.34	<	<
SO_4	100	20	.70
Cl	9.6	2.7	.48
O_2	<	.24	.23
pH	3.5	7.9	7.2

[1]Compositions of ground water used in column experiment.

[2]Ground water unaffected by the acidic plume.

Table 2. *Sorption constants for the diffuse-layer model*

[m^2/g, square meters per gram; mol/mol Fe, moles sorption sites per mole iron; LogK^{int}, log of the intrinsic surface complexation constant; $\Xi\, \mathrm{FeOH}^{o}$, ferrihydrite surface complexation site]

Ferrihydrite properties

Ferrihydrite in sediment--1 percent[1]
Specific surface area--600 m^2/g[2]
Concentration of sorption sites--0.2 mol/mol Fe[2]

Surface complexation reactions	LogK^{int} Dzombak and Morel[2]	Experi-mental[3]
(1) $\Xi\, \mathrm{FeOH}^{o} + \mathrm{H}^{+} = \Xi\, \mathrm{FeOH_2}^{+}$	[4]7.29	
(2) $\Xi\, \mathrm{FeOH}^{o} = \Xi\, \mathrm{FeO}^{-} + \mathrm{H}^{+}$	[4]-8.93	
(3) $\Xi\, \mathrm{FeOH}^{o} + \mathrm{Cu}^{2+} = \Xi\, \mathrm{FeOCu}^{+} + \mathrm{H}^{+}$	[4]0.6	
(4) $\Xi\, \mathrm{FeOH}^{o} + \mathrm{Co}^{2+} = \Xi\, \mathrm{FeOCo}^{+} + \mathrm{H}^{+}$	-3.01	[4]-2.0
(5) $\Xi\, \mathrm{FeOH}^{o} + \mathrm{Ni}^{2+} = \Xi\, \mathrm{FeONi}^{+} + \mathrm{H}^{+}$	[4]-2.5	

[1]Amount from sequential chemical extraction of uncontaminated alluvium plus amount precipitated from ground water.

[2]Dzombak and Morel (1990).

[3]Empirical fit to experimental data.

[4]Constants used in diffuse layer model.

Dzombak and Morel (1990) discuss the significant features of the diffuse-layer model and have compiled an extensive data base of thermodynamic equilibrium constants for sorption of cations and anions on $Fe(OH)_3$. Initial simulations of the experimental data used the surface area and site concentration, and the surface complexation constants from Dzombak and Morel (1990) listed in table 2. The only sorption constant that required adjustment was the LogK^{int} for Co (table 2).

After calibration of the model to the column data, changes in the aqueous composition in the aquifer were simulated with the same reactions and thermodynamic constants. The flow path chosen for the simulations connects the most contaminated well in each cluster of observation wells and is defined in figure 2 by the dashed line. Location of the plume in 1988 is defined by pH contours. Simulations consisted of modeling the changes in ground water composition between successive wells along this flow path. Simulation began at site 50 and ended at the gaging station (fig. 1). Initial and final ground water compositions are listed in table 1.

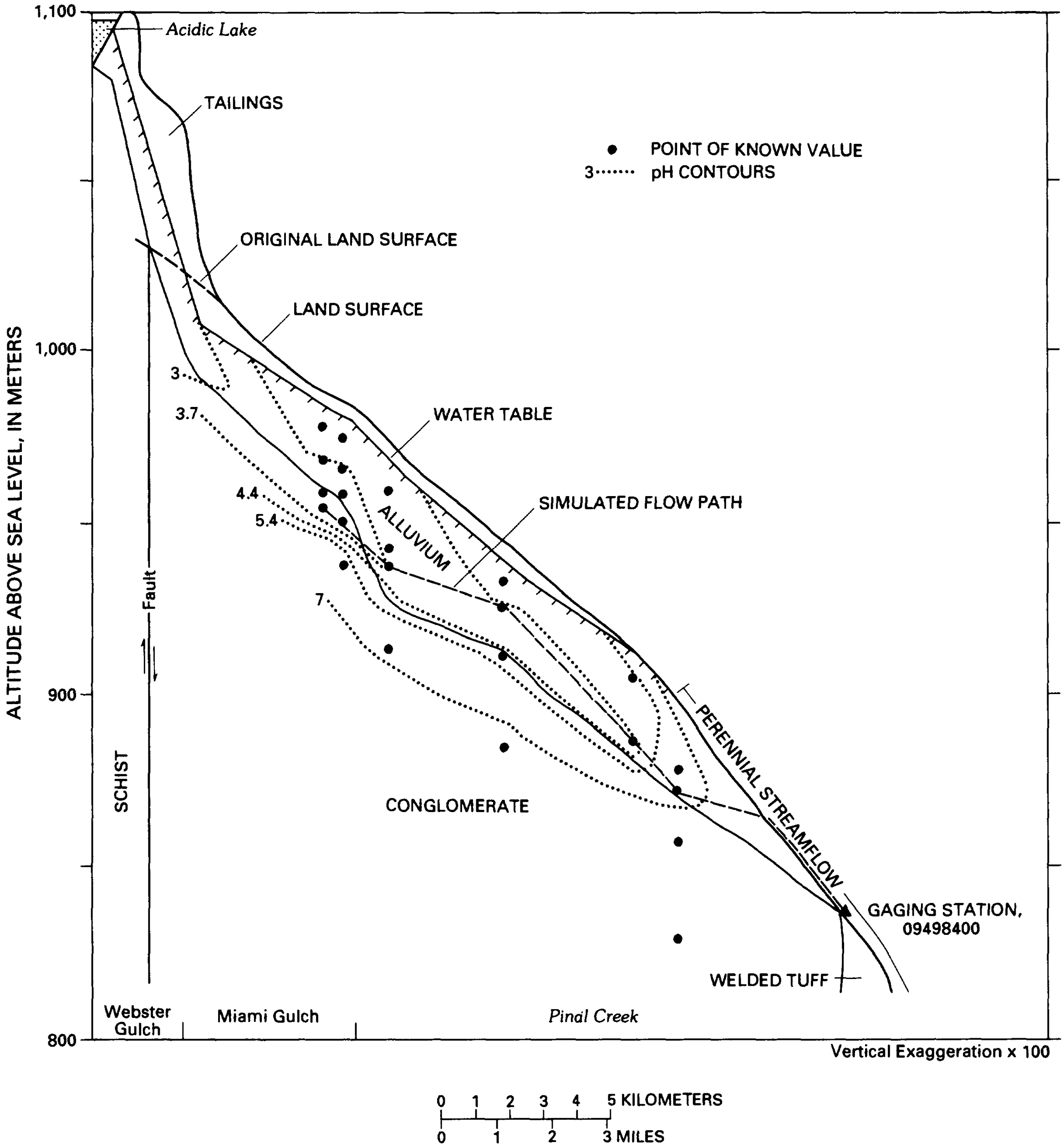
Some dilution occurs as acidic water in Webster Gulch and Miami Wash mixes with an unknown volume of ground water from Russell Gulch and Pinal Creek (fig. 1). The volume of uncontaminated ground water that mixed with acidic ground water was calculated from the decrease in Cl concentration measured between observation wells along the flow path. Dilutions were modeled with the geochemical computer program PHREEQE (Parkhurst and others, 1980), and the mixed waters were then used as input in MINTEQA2 for simulation of the sorption reactions. Reactions for all constituents in table 1 including, redox, precipitation, dissolution, and sorption were solved simultaneously. Only the results for sorption of Co, Cu, and Ni are presented here.

RESULTS AND DISCUSSION

Experimental Data

Breakthrough curves from the column experiment are plotted for Cu, Co, Ni, and pH in figure 3. Relative concentrations (effluent concentration divided by influent concentration) for Cu, Co, and Ni are plotted along the left side of the figure; measured pH is plotted along the right y-axis. One pore volume is the volume of water contained in the interstitial pore space of the column. A nonreactive solute would break through at one pore volume; breakthrough at pore volumes greater than one indicates attenuation of the solute.

Initially, reaction with carbonate minerals in the alluvium neutralized H^+ and maintained pH at approximately 8; Cu, Co, and Ni were completely removed from solution (fig. 3). After dissolution of the carbonates, pH of the effluent began to decrease and aqueous Cu, Co, and Ni increased. Sorption of Ni and Co decreased from 100 percent at pH >7 to 0 percent at pH <5. The steep slopes of the breakthrough curves for Co and Ni coincide with the rapid decrease in pH. As pH decreased to less than 5, desorption occurred and Ni and Co in the effluent increased to concentrations greater than the influent. A relative concentration of 2.4 was measured for Ni, and virtually all of the Ni sorbed between pore volumes 1 and 2 was desorbed by pore volume 5. The literature LogK^{int} of -2.5 for sorption of Ni on $Fe(OH)_3$ accurately simulated the experimental data.


1,100
1,000
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ALTITUDE ABOVE SEA LEVEL, IN METERS
Acidic Lake
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LAND SURFACE
WATER TABLE
SIMULATED FLOW PATH
ALLUVIUM
3
3.7
4.4
5.4
7
Fault
SCHIST
CONGLOMERATE
PERENNIAL STREAMFLOW
GAGING STATION, 09498400
WELDED TUFF
Webster Gulch
Miami Gulch
Pinal Creek
Vertical Exaggeration x 100
0 1 2 3 4 5 KILOMETERS
0 1 2 3 MILES

Figure 2. Generalized hydrologic section showing distribution of pH in aquifer. (Modified from Eychaner, 1989, fig. J-2).

Much of the Co was irreversibly fixed by the alluvium. The maximum concentration of Co was only 1.3 times greater than the influent concentration, and only 25 percent of the Co was desorbed. Published values of $\mathrm{LogK}^{\mathrm{int}}$ for Co of -3.01 underestimated sorption of Co, and an empirical value of -2.0 was fit to the data. The Co results suggest the possibility of an alternative reaction mechanism. Co has been correlated with Mn in soils and was fixed in a nonextractable form by replacement of Mn (III) by Co (III) whereas Cu and Ni were largely associated with iron oxides (McKenzie, 1970; 1975). In the absence of any specific chemical evidence for such a reaction in this study, Co was presumed to sorb on $Fe(OH)_3$ and the empirical $\mathrm{LogK}^{\mathrm{int}}$ was used in simulations.

Cu was not detected in effluent until the pH had decreased to 5.5. The slope of the breakthrough curve for Cu is less steep than that for Ni and Co and coincides with the decline in the rate of decrease in pH after pore volume 2.5. Cu was no longer sorbed at pH <3.5. Only 6 percent of the Cu was desorbed, a possible indication that sorption of Cu was irreversible. The $\mathrm{LogK}^{\mathrm{int}}$ for Cu of 0.6 simulated the experimental data.

Field Data

Changes in concentration of Co, Cu, Ni, and pH between Miami Wash and the gaging station are plotted in figure 4. The intrinsic equilibrium constants used to model sorption of Cu, Co, and Ni in the column experiment were also used to simulate the observed distribution along the flow path in the aquifer. Simulations began at site 50, set equal to 0 km (kilometers), and ended at the gaging station 14 km downstream. Ground water pH was less than 4.5 for the first 10 km and the diffuse-layer model predicted no sorption of Co or Ni. The observed decrease in aqueous Co and Ni between 0 and 10 km was modeled by dilution of the acidic ground water with uncontaminated ground water.

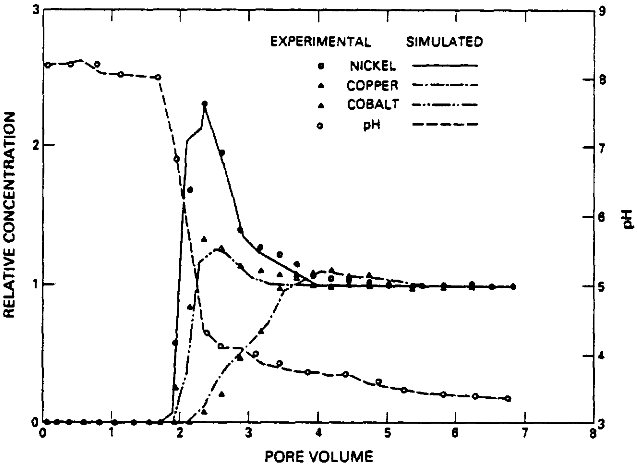

Figure 3. Column breakthrough curves for copper, cobalt, nickel, and pH: Experimental data and model simulations.

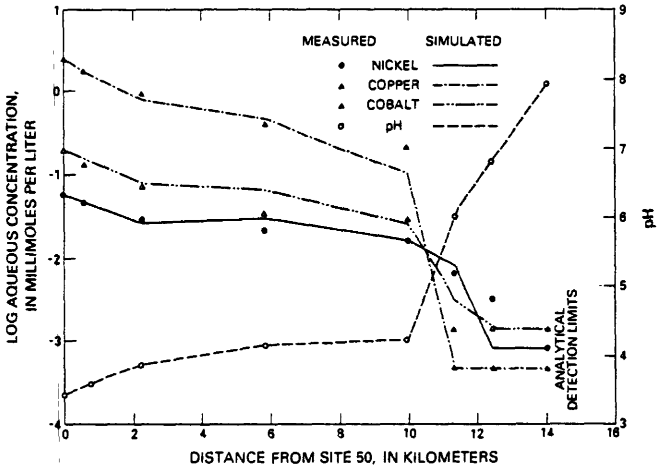

Figure 4. Measured and simulated distribution of copper, cobalt, nickel, and pH along flow path in aquifer.

The decrease in Cu over the first 10 km was simulated by a combination of dilution and sorption, consistent with the experimental data in figure 3 which indicates that Cu should sorb at pH values greater than 3.5.

The acid front of the plume where pH drops below 5 occurred between 10 and 12 km; pH increased to 6.5 and aqueous Co, Cu, and Ni decreased to near analytical detection limits. Field data were simulated reasonably well by the diffuse-layer model.

SUMMARY

Laboratory column experiments were used to evaluate reactions between acidic ground water and alluvium. The column breakthrough curves were simulated with the geochemical equilibrium speciation model MINTEQA2. Sorption of Cu, Co, and Ni was characterized by steep pH adsorption edges, where the percent sorbed changed from 0 to 100 percent over 2 pH units. Sorption reactions were quantitatively described by the diffuse- layer surface--complexation model in MINTEQA2. Ferrihydrite was the most prevalent oxide in the column alluvium and was modeled as the sorbent. Intrinsic equilibrium constants for Cu and Ni sorption on $Fe(OH)_3$ were obtained from the sorption literature: for Cu, $LogK^{int} = 0.6$; for Ni, $LogK^{int} = -2.5$. The published equilibrium constant for Co underestimated the amount sorbed in the column experiment, and an empirical $LogK^{int}$ of -2.0 was fit to the data. All of the sorbed Ni was eventually desorbed, whereas only 25 percent of the Co and 6 percent of the Cu were desorbed.

The geochemical model was then used to simulate the observed changes in concentration of aqueous constituents along a flow path in the aquifer. Attenuation of Cu, Co, and Ni along the flow path was simulated reasonably well by the diffuse-layer model with the same equilibrium constants used to model the column data.

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STABILITY AND TRANSPORT OF INORGANIC COLLOIDS THROUGH CONTAMINATED AQUIFER MATERIAL

By Robert W. Puls[1], Robert M. Powell[2], *and* Terry F. Rees[3]

ABSTRACT

Laboratory columns using contaminated natural aquifer material from Globe, Arizona, were used to investigate the transport of inorganic colloids under saturated flow conditions. Fe_2O_3 *radio-labeled spherical colloids of various diameters were synthesized and introduced into the columns under varying conditions of pH, ionic strength, electrolyte composition, and colloid concentration. Column influent and effluent were evaluated by photon correlation spectroscopy and scintillation-counting techniques. Effluent breakthrough concentrations of the colloid were as high as 57 percent of the influent concentration under certain conditions. In all cases where significant transport occurred, the colloids arrived at approximately the same time as a conservative tracer, tritium. Conditions favoring colloidal transport in this system were low ionic strength and a pH in the range where the colloids are stable. Arsenate was used as a model reactive contaminant to evaluate its facilitated transport on the* Fe_2O_3 *colloids. The calculated sorption capacity of the colloids from batch tests was 1 percent by weight for arsenate. Compared to dissolved arsenate transport in the same columns, the colloids were transported more than 21 times faster.*

INTRODUCTION

The mobility of colloidal particles (less than 10 μm (micrometers)) in ground water has been demonstrated at a number of sites (Kim and others, 1984; Robertson and others, 1984; Gschwend and Reynolds, 1987; Ryan and Gschwend, 1990). Others have demonstrated the facilitated transport of contaminants associated with reactive mobile colloidal particles in both laboratory and field studies (Saltelli and others, 1984; Enfield and Bengtsson, 1988; Buddemeier and Hunt, 1988; Penrose and others, 1990). Colloidal particles in size ranging from 0.1 to 1.0 μm may be most mobile in porous media because of diffusional and sedimentation constraints. Although Champlin and Eichholz (1976) and Cerda (1987) demonstrated that changes in the chemistry of aqueous systems may play a major role in mobilization of colloids in porous media, very little additional work has been done in this area of colloidal-transport research.

A study was conducted from March 1988 through September 1990 to assess the significance of colloidal transport in a shallow heterogeneous sand and gravel aquifer near Globe, Ariz. Field investigations initially focused on colloidal considerations in sampling ground waters for inorganic contaminants (Puls and others, 1990), and indicated the importance of pumping at low flow rates to obtain accurate and representative water-quality data. There was little evidence to suggest colloid-facilitated transport of inorganic contaminants at the site, probably because of the high ionic strength of the ground waters. Such transport may occur in lower ionic strength waters and near the leading edge of the acidic plume at the site, where pH/redox changes are most dramatic.

A laboratory-column study was initiated to investigate chemical effects on inorganic colloidal transport through contaminated aquifer material collected from different locations at the site. Variables included pH, electrolyte composition, and ionic strength. Redox changes were not evaluated because of the difficulty of controlling this variable in a laboratory setting. Radio-labeled iron oxide (Fe_2O_3) was used as the model mobile reactive colloid. Arsenate was investigated as a potentially reactive and transportable contaminant. This paper summarizes the results of the study and, in particular, its implications for the significance of colloidal-facilitated contaminant transport at the Globe, Ariz., site.

STUDY SITE

The study site is located at Pinal Creek, near Globe, Ariz., about 130 km (kilometers) east of Phoenix and about 170 km north of Tucson. Copper has been mined since 1903 from granite porphyry adjacent to an aquifer at the site. A band of unconsolidated alluvium 300 to 800 m (meters) wide, as much as 50 m thick and about 20 km long, forms the upper, central part of the aquifer in a valley along Miami Wash and Pinal Creek (fig. 1). Most of the sediment in the alluvium ranges in size from fine sand to coarse gravel, but clay lenses and boulders are also present. Alluvial, consolidated, basin fill, greater than 100 m thick, forms the remainder of the aquifer beneath and adjacent to the unconsolidated alluvium.

In the upper alluvium, hydraulic conductivity is on the order of 200 m/d (meters per day) on the basis of cross-sectional area, hydraulic gradient, and measured outflow (C.C. Neaville, U.S. Geological Survey, written commun., 1990). On the basis of hydraulic gradients that range from 0.005 to 0.008 and an assumed porosity of 0.3, the calculated average linear ground-water flow velocities near the wells in the upper alluvium range from 0.3 to 3 m/d.

MATERIALS AND METHODS

Spherical, monodisperse Fe_2O_3 colloids (100-250 nanometers) were prepared from solutions of $FeCl_3$ and HCl using the method of Matijevic and Scheiner (1978). The method was modified by the addition of a spike of ${}_{26}Fe^{59}Cl_3$, prior to heating, permitting detection of the colloid using liquid scintillation-counting techniques. The colloids were

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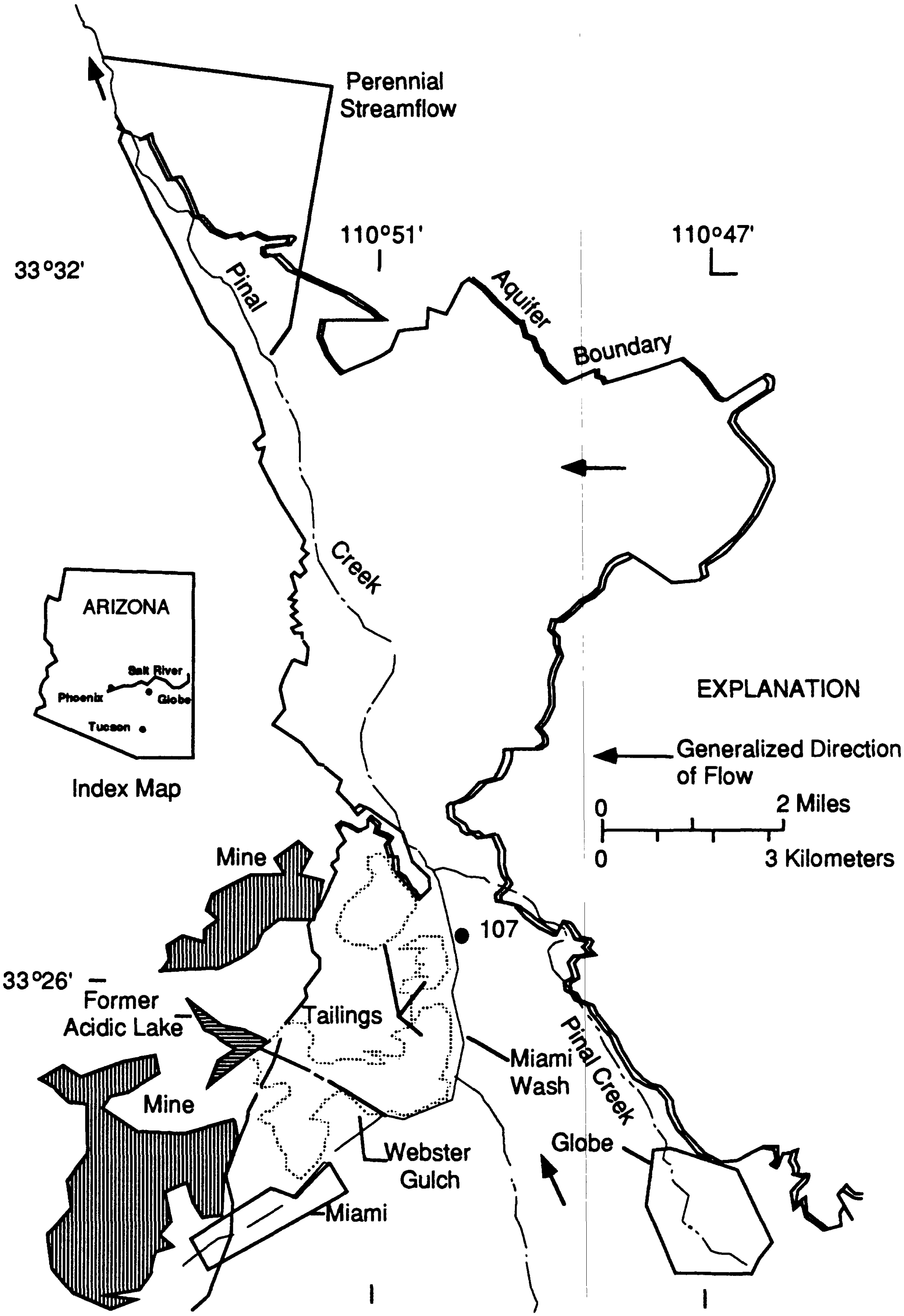
Perennial Streamflow
110°51'
110°47'
33°32'
Pinal
Aquifer
Boundary
Creek
ARIZONA
Salt River
Phoenix
Globe
Tucson
Index Map
EXPLANATION
Generalized Direction of Flow
0
2 Miles
0
3 Kilometers
Mine
107
33°26'
Former Acidic Lake
Tailings
Miami Wash
Pinal Creek
Mine
Webster Gulch
Miami
Globe

Figure 1. Plan view of study site (modified from Puls and others, 1990).

washed repeatedly with pH 3 deionized water to remove unreacted materials from the suspensions. Colloid concentration, in milligrams per liter, was determined by both filtration and residue on evaporation techniques. Scanning electron microscopy (SEM) and photon correlation spectroscopy (PCS) were used to determine the particle size. PCS was also used to evaluate stability of the diluted colloidal suspensions and particle size in both influent and effluent column suspensions.

The pH of zero point of charge (pH_{zpc}) is the pH at which the net surface charge of the colloid equals zero. Below this value, the surface maintains a net positive charge, whereas above the pH_{zpc}, a net negative charge results. The pH_{zpc} was determined by titrating colloid suspensions under nitrogen at different ionic strengths of $NaClO_4$, a nonspecifically adsorbed electrolyte, with NaOH. The pH at which electrolyte concentration has no influence on surface charge should equal the pH_{zpc}. For the Fe_2O_3 colloids this was estimated to be in the pH range 7.3 to 7.6.

Core material from well 107 was used to pack the 2.5-centimeter diameter, adjustable, glass columns. Column flow rates used were comparable to estimated ground water velocities in the alluvium. Prior to packing, the core sample was air-dried and sieved with the fraction between 106 and 2000 µm used in the columns. Subsamples were analyzed by x-ray diffraction. The predominant mineral phases identified in order of intensity, were: quartz > albite >> magnesium orthoferrosilate > muscovite >> manganese oxide. Most aquifer materials carry a net negative surface charge under most natural environmental conditions, due to the predominance of silica ($pH_{zpc} \sim 2$) and aluminosilicates in their matrix. Manganese oxide phases also have low pH_{zpc}'s (<4.5). Relevant aqueous geochemical parameters for well 107 are listed in table 1.

Table 1. *Major cation/anion concentrations and water-quality indicators for well 107, March 1989*

[Concentrations, in milligrams per liter; µS/cm, microsiemens per centimeter at 25 °Celsius; C, degrees Celsius; mv, millivolts; mol/L, moles per liter]

Ca	440	pH	3.72
Mg	140	Specific conductance (µs/cm)	4,310
Na	140	Temperature (µC)	18.5
K	7.2	Dissolved O_2 (mg/L)	<0.1
SO_4	3,300	Oxid-red. pot. (mv)	440
Cl	33	Ionic strength (mol/L)	0.13

RESULTS AND DISCUSSION

Batch Tests

Data for arsenate sorption on the synthesized iron oxide colloids were fitted to a Langmuir isotherm defined by the relation $S = (k(Cf)b)/(1 + k(Cf))$, where k is the Langmuir solid surface affinity term, b the adsorption capacity, S the concentration on the solid phase, and Cf the steady-state solution concentration. One advantage of the Langmuir model is the incorporation of the capacity term. The correlation coefficient for the linearized Langmuir form of the above equation was 0.97 and the b-value 0.01 gram per gram, or 1 percent of the colloid mass is sorbed arsenate.

Stability

Colloid stability, in terms of coagulation, was monitored using laser light scattering with photon correlation spectroscopy. The colloid suspensions were stable up to 0.01 M (molar) in NaCl, $CaCl_2$, and $NaClO_4$ from pH 3.0 to 6.5 (colloids net positively charged). From pH 6.5 to 7.6, near the estimated pH_{zpc}, the colloids were extremely unstable. From pH 7.6 to 9.7 they were quasi-stable up to 0.005 M in NaCl and $NaClO_4$, that is, the kinetics of coagulation were slow (several hours). In the pH region from 9.7 to 11.0 the colloids were stable up to 0.01 M in $NaClO_4$ and NaCl. In cases where the soil column effluent solution pH was as low as 7.6--that is, in a region of relative instability, colloidal size distributions in the influent and effluent were compared.

Liang and Morgan (1990) observed that hematite colloids bear an overall net negative charge at pH << $pK_{zpc,pristine}$ in the presence of specifically sorbed anions (for example, phosphate species), increasing the stability region where the colloids are negatively charged. Similarly, significant enhancement of colloid stability by 0.01 M Na_2HAsO_4 was observed in the present study at pH as low as 6.9 (< pristine pH_{zpc}). Attempts to duplicate this with sulfate were generally unsuccessful. Only quasi-stable suspensions were obtained on the negative side of the pH_{zpc} of the colloids. These findings have important implications for the Globe site, where sulfate is as high as 0.09 M near the source of contamination and about 0.03 M at well 107.

Table 2. *Colloidal transport through contaminated aquifer material*

[Nm, nanometers; mg/L, milligrams per liter; m/d, meters per day; $\%_oC_o$, percent initial concentration colloids]

Size (nm)	Part. conc. (mg/L)	Flow rate (m/d)	pH	Ionic strength	Anion	C_{max} ($\%_oC_o$)
200	10	3.4	3.9	0.005	Cl-	0
125	10	1.7	8.9	0.005	Cl-	54
150	5	1.7	8.1	<0.001	ClO_4^-	57
250	10	1.7	8.1	0.03	SO_4^{2-}	17
150	5	1.7	8.9	0.03	SO_4^{2-}	14

Column Tests

The results of various column experiments are listed in table 2. When the colloids had a net positive charge, virtually opposite to that of the column matrix material, there was no transport of the colloids through the columns. When these columns were dismantled, most of the colloids were at the inlet. When the colloids were net negatively-charged (pH > pH_{zpc}), significant transport was observed in NaCl and $NaClO_4$. More than 50 percent of the injected colloids were detected in the effluent. In the case of sulfate, significantly less was transported presumably due to colloidal instability. In all cases, breakthrough occurred at approximately the same time as a conservative tracer, tritium (figs. 2a-b).

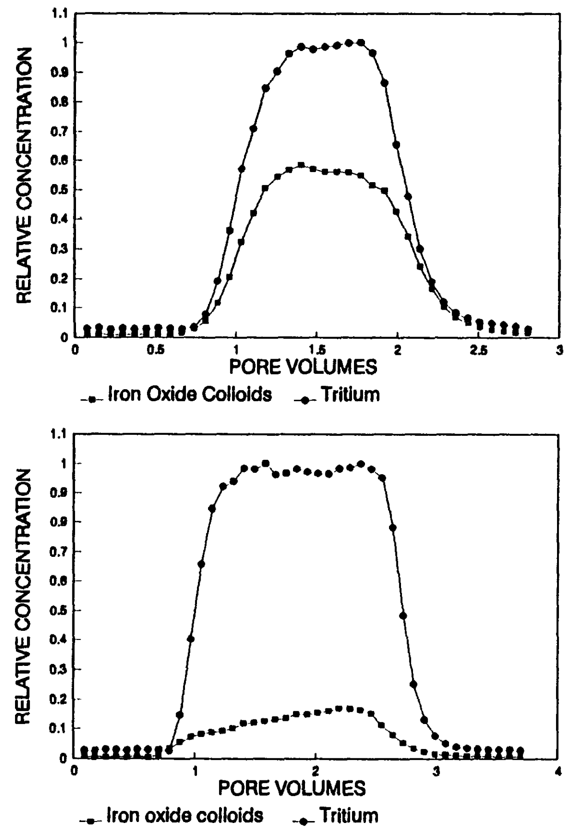

Figure 2. Breakthrough curves: a) top, <0.001 molar $NaClO_4$, pH 8.1, 150 nanometer colloids; b) bottom, 0.01 molar Na_2SO_4, pH 8.1, 250 nanometer colloids.

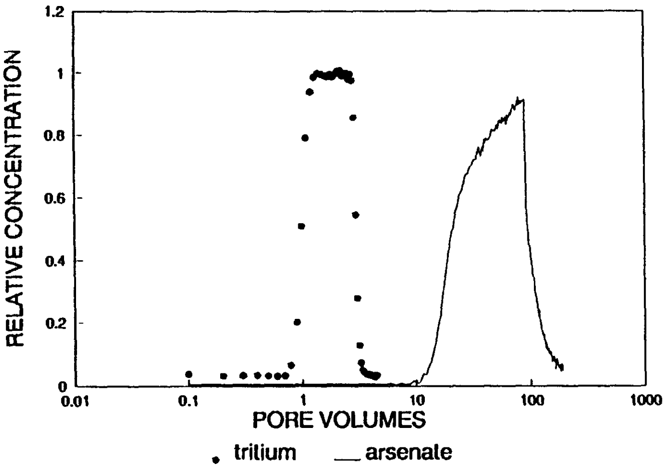

Figure 3. Transport of dissolved arsenate in 0.01 molar $NaClO_4$, 1.7 meters per day, pH 8.1.

A column was also run with dissolved arsenate to compare its retardation with that of the colloids. Figure 3 shows the breakthrough curve relative to tritium (or the Fe_2O_3 colloids). The calculated retardation factor or Rf, defined as Rf = V_w/V_s, where V_w is the velocity of the water or conservative tracer, and V_s is the velocity of the solute, was 21. The colloids, whose breakthrough occurred the same time as the tritium, also exhibited 21 times the velocity of the dissolved arsenate.

SUMMARY AND CONCLUSIONS

The Fe_2O_3 colloids used in this study are capable of sorbing a significant mass of contaminant (arsenate) and were transported more than 21 times faster than dissolved arsenate under some hydrochemical conditions. Significant transport of the Fe_2O_3 colloids was obtained in relatively low ionic-strength waters, at high flow velocity, and when the colloids' net surface charge was similar (negative) to that of the aquifer matrix. Electrolyte composition was important, with sulfate providing the least stable suspensions and lowest colloid throughput. This is significant for the Globe site, where sulfate is the predominant anion in the ground water. This, together with the high ionic strength of most waters at the site, suggests colloidal transport does not significantly facilitate transport of contaminants at the site.

DISCLAIMER

Although the research described in this article has been funded wholly or in part by the U.S. Environmental Protection Agency, it has not been subjected to the Agency's peer and administrative review and therefore may not necessarily reflect the views of the Agency and no official endorsement may be inferred.

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GROUND-WATER TRANSPORT OF POLYCYCLIC AROMATIC HYDROCARBONS IN ASSOCIATION WITH HUMIC SUBSTANCES IN THE PINAL CREEK BASIN, GLOBE, ARIZONA

By Robert W. Wallin[1], R.L. Bassett[1], *and* James H. Eychaner[2]

ABSTRACT

Polycyclic aromatic hydrocarbons are present in ground water in the Pinal Creek basin near Globe, Arizona. The maximum concentration of quantified polycyclic aromatic hydrocarbons in samples from monitoring wells was 35 micrograms per liter. Polycyclic aromatic hydrocarbon contamination was found in a plume about 11 kilometers long. The source probably is in an area of active mining operations several kilometers upstream from the sampled wells. Concentrations of quantified polycyclic aromatic hydrocarbons in the aquifer decrease significantly as the pH rises above 4. Concentrations of dissolved organic carbon decrease in the same area. The fractions of the dissolved organic carbon that decrease are predominantly dissolved humic substances. Analyses of the data indicate that partitioning of polycyclic aromatic hydrocarbons onto dissolved humic substances could be occurring and the removal of polycyclic aromatic hydrocarbons could be controlled by the adsorption of dissolved humic substances onto metal hydroxides.

INTRODUCTION

Contamination of an aquifer by acidic water in a copper-mining district near Globe, Ariz. (fig. 1), has produced a plume 17 km (kilometers) long (Eychaner, 1991, this Proceedings). Eychaner also describes the study area and overall project objectives. The aquifer consists of an upper alluvial unit and underlying basin fill. Dissolved organic carbon (DOC) in samples from monitoring wells in the plume was as much as eight times the background concentration (Reese and Bassett, 1990). The fraction of humic substances in the DOC is only about 25 percent, indicating that substantial amounts of organic contaminants are present with the inorganic contaminants (Reese and Bassett, 1990). An anthropogenic source for the remaining DOC is suspected because of the small amount of vegetation in the streambed and the low fraction of organic carbon adsorbed onto the aquifer material.

Water samples were collected on 4 trips during 1989-90 from 25 wells to examine the distribution and fate of polycyclic aromatic hydrocarbons (PAH) in the aquifer system. PAH detected in 14 wells define a plume extending from well site 050 to well site 500 (fig. 1). Total quantified concentration of PAH at well 051 was 35 μg/L (micrograms per liter). Samples were collected from monitoring wells constructed with solvent-welded polyvinyl chloride casing. A PAH source in the well materials is unlikely because the wells generally were in service more than 3 years and were thoroughly purged before sampling. PAH were extracted from samples by hydrophobic adsorption in a column containing C-18 bonded porous silica, then eluted with solvent. Gas chromatography mass spectrometry was used to identify and quantify the PAH. This paper describes PAH contamination in the aquifer and discusses relevant transport mechanisms.

ANALYTICAL RESULTS

PAH were found in water from 14 of the 25 wells sampled (table 1). Twelve compounds were identified. Six of the compounds were quantified by comparison to a 16-compound standard solution and 6 were not quantified. Identified PAH compounds define a plume from the upper part of the basin fill in the upgradient part of the study area to the lower part of the alluvium downgradient (fig. 2). Upgradient and downgradient limits of the plume have not been defined. Quantified PAH concentrations decrease to less than 0.1 μg/L in samples for which pH exceeds 4. DOC concentrations decrease in the same pH area. The fractions of DOC that decrease are predominantly dissolved humic substances (DHS) (Reese and Bassett, 1990).

Average recoveries from standards for eight PAH ranged from 66.9 to 116.5 percent. Standard deviations ranged from 17.6 to 34.1 percent. Well locations and concentrations of DOC, pH, and PAH are listed in table 2.

TRANSPORT PROCESSES

Humic substances can enhance the solubility of organic micropollutants in ground water. Humic substances can act as chelating agents for organic compounds, greatly increasing their solubility and affecting their mobilization and transport (Carlberg and Martinsen, 1982). Hydrogen bonding appears to play a major role in the complexation of organic material to DHS. Furthermore, reaction rates between DHS and PAH were large and equilibria were reached quickly (Carlberg and Martinsen, 1982). At low DHS concentrations, partition coefficients for binding of PAH onto DHS were determined to be approximately equal to the octanol-water partition coefficients (K_{ow}) of three PAH studied (Landrum and others, 1984). Chiou and others (1987) found partitioning of organic micropollutants to soil-derived humic acids to be proportionate with K_{ow}; however, degree of solubility enhancement was found to be dependent on DHS molecular size and polarity. The binding of one PAH (pyrene) to DHS was found to be modified by the degree of aromaticity in the DHS (Gauthier and others, 1987). Because of the different binding properties of different DHS and because DHS represent a mixture whose composition is not consistent from one location to another, precise quantification of solubility enhancement is difficult.

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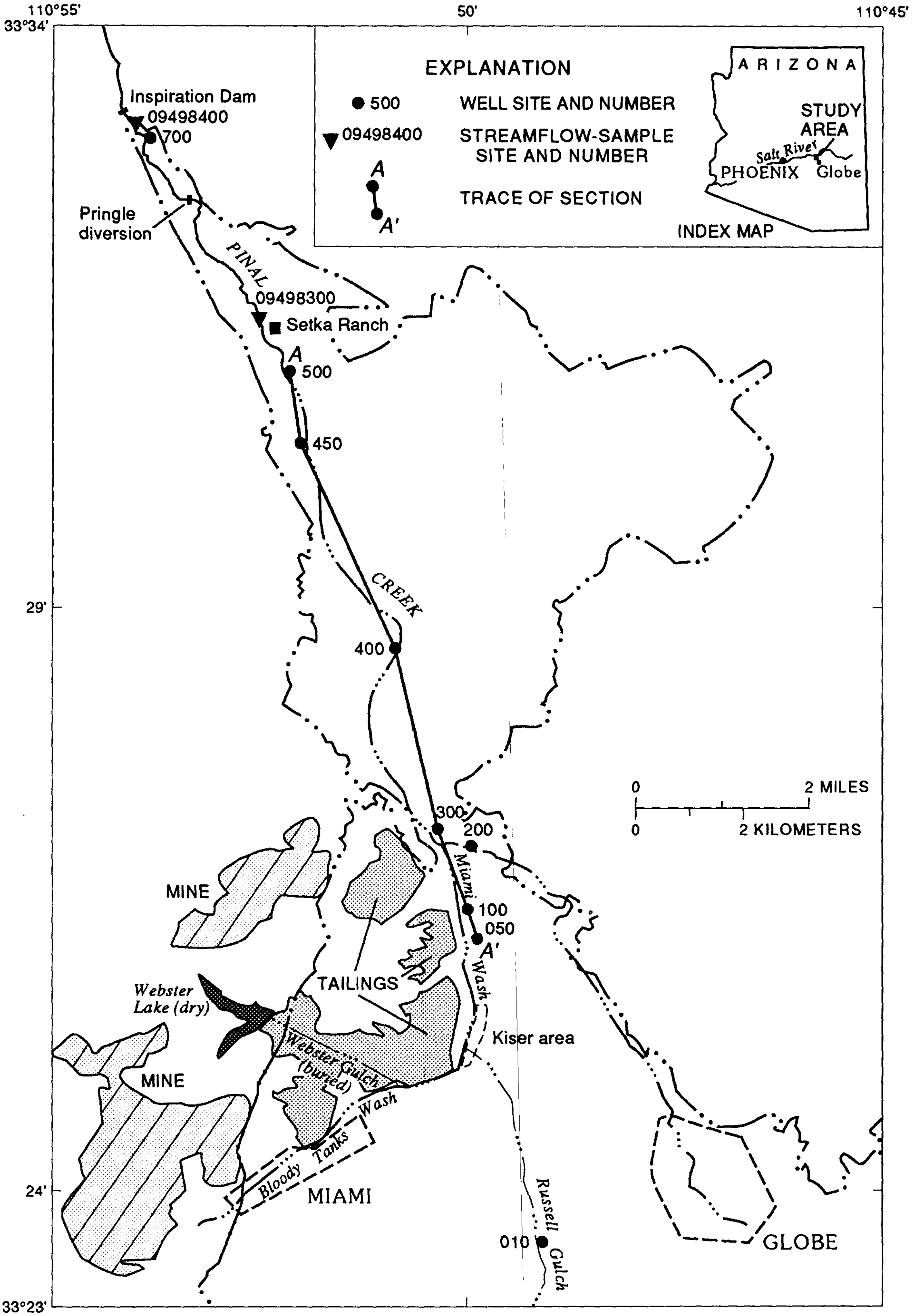

110°55'
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EXPLANATION
● 500 WELL SITE AND NUMBER
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A
A'
TRACE OF SECTION
ARIZONA
STUDY AREA
Salt River
PHOENIX
Globe
INDEX MAP
Inspiration Dam
09498400
700
Pringle diversion
PINAL
09498300
Setka Ranch
A
500
450
CREEK
400
300
200
Miami
100
050
A'
Wash
0
2 MILES
0
2 KILOMETERS
MINE
TAILINGS
Webster Lake (dry)
Webster Gulch (buried)
Kiser area
MINE
Wash
Bloody Tanks
MIAMI
Russell Gulch
010
GLOBE

Figure 1. Area of study.

Table 1. *Concentrations of polycyclic aromatic hydrocarbons, Pinal Creek basin, Globe, Arizona, 1989-90*

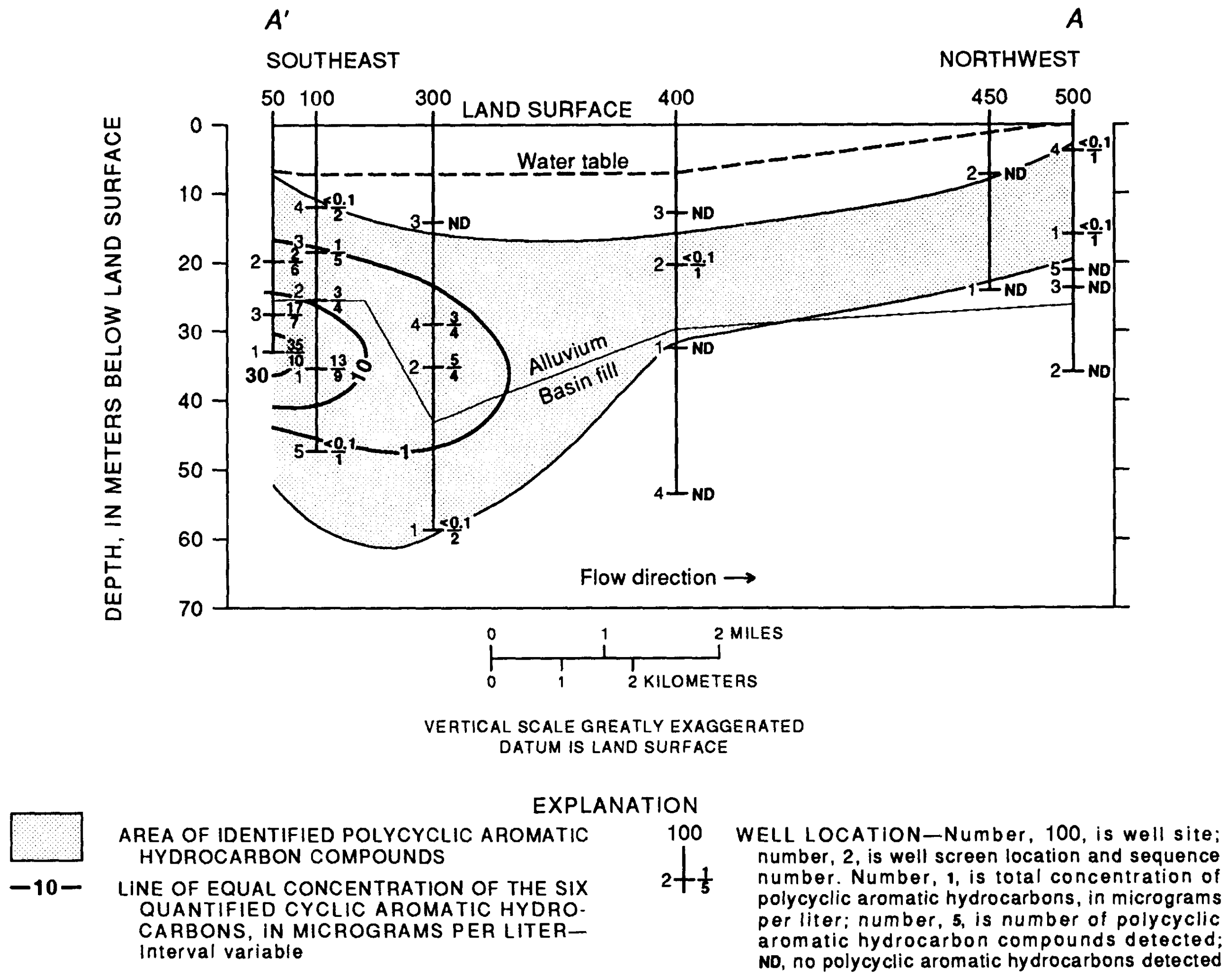
[Concentrations, in micrograms per liter. X, indicates detected but not quantified. Dashes indicate analyzed for but not detected]

Compound	Molecular weight	051 5/90	052 5/90	053 5/89	101 5/90	102 5/89	103 3/89	104 6/88	105 3/89	301 5/90	302 2/90	304 5/90	402 5/89	501 3/89	506 3/89
		Well number and date sampled													
Naphthalene	(128)	16.21	1.35	8.32	7.27	1.78	0.43	--	--	--	3.11	--	--	--	--
Acenaphthene	(154)	12.09	.80	5.42	4.17	1.26	.35	--	--	--	2.03	1.63	--	--	--
Fluorene	(166)	3.62	1.81	.90	--	--	--	--	--	--	--	1.53	--	--	--
Phenanthrene	(178)	1.07	--	.60	--	--	--	--	--	--	--	--	--	--	--
Acenaphthylene	(152)	.62	--	.31	.26	--	--	--	--	--	--	--	--	--	--
Anthracene	(178)	1.06	--	--	--	--	--	--	--	--	--	--	--	--	--
Methylnaphthalene	(142)	X	X	X	X	X	[1]X	--	--	X	X	[1]X	--	--	--
Dimethylnaphthalene	(156)	X	X	X	X	X	--	--	--	X	X	[1]X	--	--	--
Dimethylisopropyl-naphthalene[2]	(198)	--	--	--	X	--	--	--	--	--	--	--	X	X	X
Methylbiphenyl[3]	(168)	[1]X	--	--	X	--	X	[1]X	[1]X	--	--	--	--	--	--
Dibenzofuran	(168)	X	[1]X	--	--	--	--	--	--	--	--	--	--	--	--
Isobenzofurandione	(148)	--	[1]X	--	X	--	X	[1]X	--	--	--	--	--	--	--

[1] Probability of identification less than 50 percent.

[2] Identified as dimethylisopropylnaphthalene or ethylphenoxybenzene.

[3] Identified as methylbiphenyl, propenylnapthalene, or methylenebisbenzene.


A'
SOUTHEAST
A
NORTHWEST
50
100
300
LAND SURFACE
400
450
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Water table
Alluvium
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Flow direction →
DEPTH, IN METERS BELOW LAND SURFACE
0
10
20
30
40
50
60
70
ND
<0.1
0 1 2 MILES
0 1 2 KILOMETERS
VERTICAL SCALE GREATLY EXAGGERATED
DATUM IS LAND SURFACE
EXPLANATION
AREA OF IDENTIFIED POLYCYCLIC AROMATIC HYDROCARBON COMPOUNDS
—10— LINE OF EQUAL CONCENTRATION OF THE SIX QUANTIFIED CYCLIC AROMATIC HYDROCARBONS, IN MICROGRAMS PER LITER—Interval variable
100
WELL LOCATION—Number, 100, is well site; number, 2, is well screen location and sequence number. Number, 1, is total concentration of polycyclic aromatic hydrocarbons, in micrograms per liter; number, 5, is number of polycyclic aromatic hydrocarbon compounds detected; ND, no polycyclic aromatic hydrocarbons detected

Figure 2. Generalized hydrogeologic section showing distribution of total quantified polycyclic aromatic hydrocarbons in the aquifer, Pinal Creek basin, Globe, Arizona, 1989-90.

Table 2. *Concentrations of dissolved organic carbon, pH, and total quantified polycyclic aromatic hydrocarbons, Pinal Creek basin, Globe, Arizona, 1989-90*

[Dashes indicate well was not sampled. < , less than analytical detection limit]

Well number	Dissolved organic carbon, in milligrams per liter[1]	pH[2]	Total quantified polycyclic aromatic hydrocarbons, in micrograms per liter
010	1.1	6.91	<0.1
051	4.2	3.65	35
052	2.3	[3]3.82	2.2
053	3.3	3.64	17
054	1.9	3.83	--
101	3.3	3.69	13
102	2.5	3.68	3.0
103	2.3	3.73	.78
104	1.4	4.01	<.1
105	1.6	6.51	<.1
201	.7	7.06	<.1
202	.7	--	--
301	.7	[3]6.71	<.1
302	1.1	[3]3.90	5.1
303	1.3	4.19	<.1
304	--	[3]4.00	3.2
401	.5	4.60	<.1
402	1.8	4.07	<.1
403	1.2	4.63	<.1
404	.3	7.41	<.1
451	--	4.26	<.1
452	--	5.40	<.1
501	1.1	5.92	<.1
502	.1	7.34	<.1
503	1.1	5.82	<.1
504	.5	7.59	--
505	--	6.11	<.1
506	1.8	5.96	<.1

[1] Data from Reese (1989).

[2] Data from Brown (1990).

[3] Data from Eychaner and others (1989).

PAH generally have no net charge. Biodegradation of PAH by oxidation, however, forms hydroxyl and carboxyl functional groups that increase PAH solubility. Bacteria species that use PAH as a sole substrate have been identified. Naphthalene can be metabolized by Cunninghamella and Pseudomonas bacteria (Davies and Evans, 1964; Gibson, 1978). Phenanthrene and anthracene can be metabolized by Pseudomonas (Evans and others, 1965). However, no oxidized PAH were detected in the upgradient part of the study area where the pH is below 4. Adsorption of organic material onto DHS decreases PAH availability to microbial degradation (J.T. Novak, Virginia Polytechnic Institute and State University, written commun., 1990). Thus, biodegradation probably is not a significant process because of (1) the refractory nature of the compounds, (2) the low pH, and (3) the absence of oxidation products.

The breakthrough for conservative inorganic species, such as chloride, has already passed through the study area. The remaining plume of low pH water between well sites 050 and 500 defines a reaction zone of acid neutralization. The reaction zone front is migrating slowly downgradient as the acid-neutralizing capacity of the aquifer matrix is depleted. Coincident with this reaction zone is the area of elevated DOC and PAH. The close association of DOC and PAH with pH is unusual; DOC generally is conservative in alluvial aquifers with low fractions of organic carbon such as is observed in this system.

Dilution and reaction contribute to the decrease in DOC downgradient. About 72 percent of the DOC decrease can be attributed to dilution (Reese and Bassett, 1990). The remaining fraction probably is lost from the system by adsorption as evidenced by the coincidence of loss in DOC and the appearance of hydroxides of iron and aluminum at the pH reaction zone front. Iron and aluminum are in solution in the upgradient part of the study area where the pH is below 4 (Eychaner and Stollenwerk, 1985). Downgradient, where the pH rises above 4, iron hydroxide [$Fe(OH)_3$] and aluminum hydroxide ($Al(OH)_3$) precipitate. In the pH range of 4 to 6, the surfaces of iron and aluminum hydroxides have a positive charge (Thurman, 1985). DHS have numerous carboxyl groups that contribute to their hydrophilic character and dissociate between pH 2 and 6. DHS containing carboxyl groups become increasingly more negatively charged below pH 6 and would be sorbed onto metal hydroxides.

The DOC being lost through adsorption is primarily from the hydrophobic acid and hydrophilic fractions--the major components of DHS (Reese and Bassett, 1990). A decrease in DOC concentration of about 28 percent after accounting for dilution occurs where pH in the aquifer exceeds 4 (Reese, 1989). Adsorption of DHS onto iron hydroxide and aluminum hydroxide surfaces probably is occurring. No evidence of PAH oxidation or adsorption directly onto metal hydroxides was observed; however, DOC with hydrophilic character that has sorbed onto metal hydroxide surfaces in the area of the pH front also has a hydrophobic component that could provide an excellent surface onto which the PAH would easily partition. The transport of PAH could be facilitated by the migration of DHS, such that most of the PAH are actually partitioned into, or sorbed onto, the DHS. As the hydrophilic fraction of the DOC sorbs, the incorporated PAH would be sorbed as well. This mechanism is postulated to explain the coincidence of decreases in DOC and PAH.

The detection of PAH in the samples as distinct molecules could be a result of the extraction process. The column has a strong hydrophobic character that can separate the PAH from its cotransporting material. This process is the subject of further investigation and illustrates the potential for significant migration of nonionized hydrophobic micropollutants, especially in areas with elevated DOC. Removal of DOC at the pH front near Globe is an unusual circumstance brought about as a result of metal hydroxide formation; the process is not common in ground water.

SUMMARY

PAH were found as contaminants in ground water in the Pinal Creek basin near Globe, Ariz. The largest concentration of total quantified PAH, found in water from a well in the upgradient part of the study area, was 35 µg/L. Of 25 wells sampled, 14 contained detectable PAH. A plume of PAH was delineated that extended the entire length of the study area, a distance of about 11 km. The axis of the plume is in the upper part of the basin fill in the upgradient part of the study area and in the lower part of the alluvium in the downgradient part.

Quantified PAH concentrations decrease in the area of the aquifer where the pH increases above 4, and DOC concentrations decrease in the same area. At low DHS concentrations, partition coefficients for binding of PAH onto DHS have been determined to be approximately equal to the K_{OW}. DHS probably are adsorbing onto metal hydroxides, which began to precipitate out of solution above pH 4. As neutral substances, PAH would not be expected to be sorbed to metal hydroxide surfaces, but partitioning of PAH onto DHS could be occurring. Thus, the removal of PAH from the aquifer could be controlled by the adsorption of DHS onto metal hydroxides. Additional study of this system is needed to fully substantiate this hypothesis.

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HYDROCHEMICAL ZONING IN THE PINAL CREEK ALLUVIUM

By Gary R. Walter[1] *and* James R. Norris[1]

ABSTRACT

Acidic water is present in the alluvial aquifer along Pinal Creek near Globe, Arizona, as a result of mining and mineral processing in the Globe Mining District. Vertical and lateral variations in lithology and water chemistry were defined at four cross sections in the Pinal Creek alluvial valley on the basis of samples collected from boreholes drilled by the dual-wall, casing-hammer technique. Analyses of these samples show that the most acidic water is confined to the lower part of the alluvium. Large differences in pH may result from density stratification and neutralization reactions. Neutralized water is present throughout the alluvium, and differences in dissolved solids concentration result primarily from dilution by recharge waters.

INTRODUCTION

Acidic, metal-bearing ground water is present in the alluvial aquifer along Miami Wash and Pinal Creek near Globe, Ariz. (fig. 1). The chemical composition of ground water in the alluvial aquifer is spatially variable as a result of chemical reactions between the dissolved constituents in the water and the alluvium, aqueous-phase reactions within the water, and physical mass-transport processes. As a result of these processes, the chemical composition of the ground water is variable vertically, laterally, and longitudinally within the aquifer.

Defining and understanding the spatial distribution of the hydrochemical facies within the alluvial aquifer is important to the design of a cost-effective remedial action plan for the aquifer. To this end, specialized drilling, sampling, and well construction methods were used during the remedial investigation to define vertical and horizontal variability in water chemistry within the alluvial aquifer. This paper briefly describes the results of these investigations. More detailed descriptions of the hydrology, geology, and longitudinal variations in hydrochemistry of the study area are presented in Eychaner and Stollenwerk (1985), Eychaner (1989), and Hydro Geo Chem, Inc., (1989).

HYDROGEOLOGIC BACKGROUND

The alluvial aquifer consists of unconsolidated sediment deposited in stream channels incised into the indurated Gila Conglomerate along the Miami Wash and Pinal Creek drainage. The alluvium consists of detritus of igneous, metamorphic, and sedimentary rocks derived from the surrounding uplands. These sediments are in the form of lensoidal deposits of sand and gravel with cobble zones and sporadic beds of calcareous clay. The sediments are generally coarsest near the base of the alluvial aquifer. The thickness of the alluvium ranges from about 35 m (meters) in Miami Wash to less than a meter at Inspiration Dam. The width of the alluvium ranges from 300 to 600 m. The underlying conglomerate has a calcareous cement and is much less permeable than the alluvium.

METHODS

The most useful data for defining vertical and lateral variations in the lithology and water chemistry within the alluvial aquifer were obtained from monitoring wells constructed at four sections across the alluvial valley. The locations of these sections, designated Nugget Wash, Wheatfields, Sunflower Ranch, and Leading Edge, are shown in figure 1. The boreholes for the monitoring wells shown in these sections were drilled using the dual-wall, casing hammer method (Strauss and others, 1989). This drilling technique yielded representative sediment samples and allowed water samples to be bailed from selected depths as the borehole was advanced. The pH and specific conductance of fluid samples, which were bailed from the drive-casing after purging with air, were measured in the field.

RESULTS

Figures 2 and 3 show variations in lithologies, pH, and specific conductance in the Nugget Wash and Leading Edge geologic and hydrogeologic sections. These sections illustrate that water with the lowest pH and the highest dissolved-solids concentrations is near the base of the alluvium. The pronounced vertical and lateral variability in pH, seen in all of the sections, are believed to result from density stratification and neutralization reactions with the residual carbonate in the alluvium. The variations in specific conductance are more subdued and result primarily from mixing of neutralized water (with a high residual dissolved-solids concentration) with recharge waters.

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[1] Hydro Geo Chem, Inc., Tucson, Ariz.

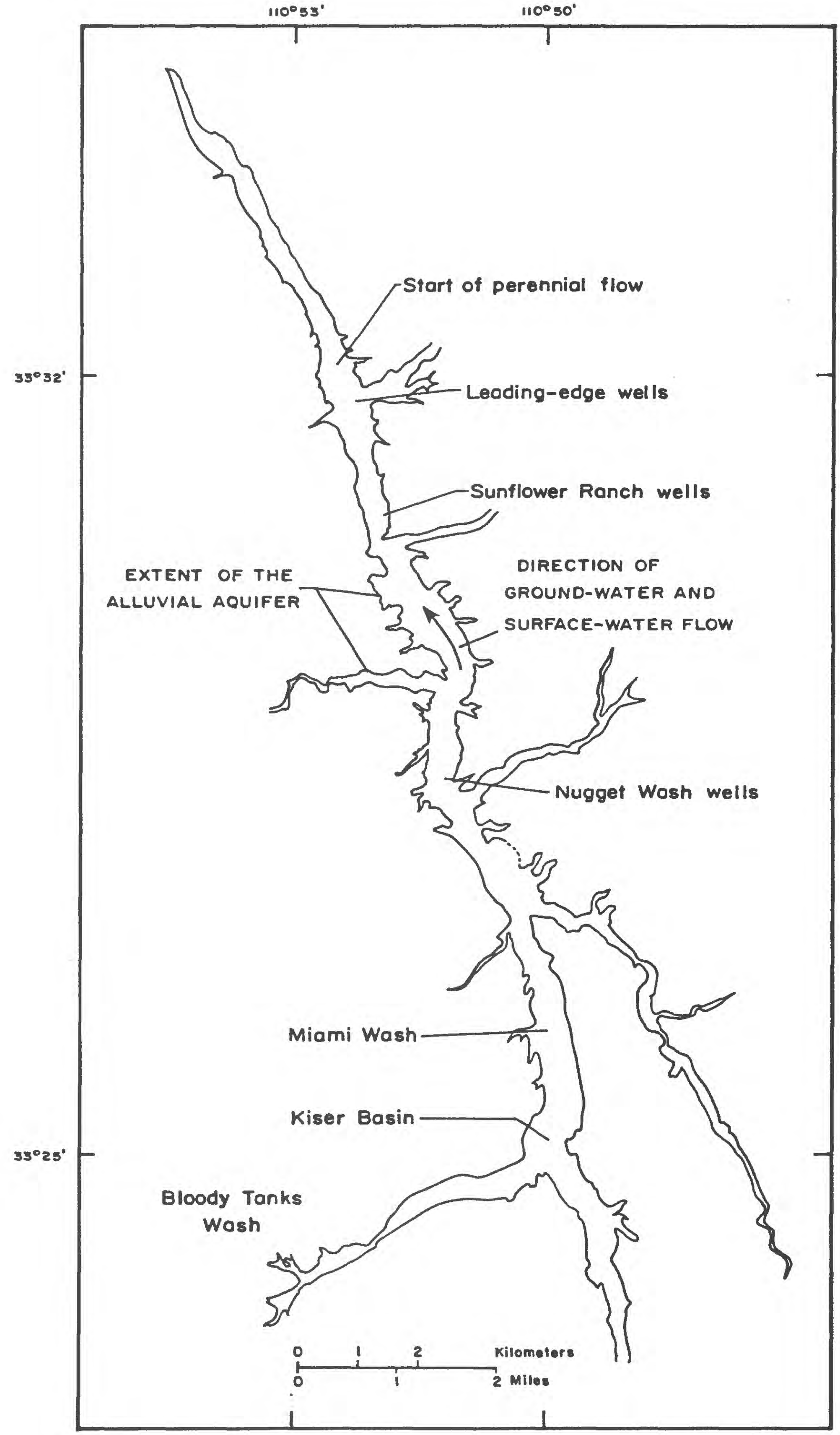
110°53'
110°50'
33°32'
33°25'
Start of perennial flow
Leading-edge wells
Sunflower Ranch wells
EXTENT OF THE ALLUVIAL AQUIFER
DIRECTION OF GROUND-WATER AND SURFACE-WATER FLOW
Nugget Wash wells
Miami Wash
Kiser Basin
Bloody Tanks Wash
0 1 2 Kilometers
0 1 2 Miles

Figure 1. Location map showing alluvial aquifer and locations of key monitoring well profiles.

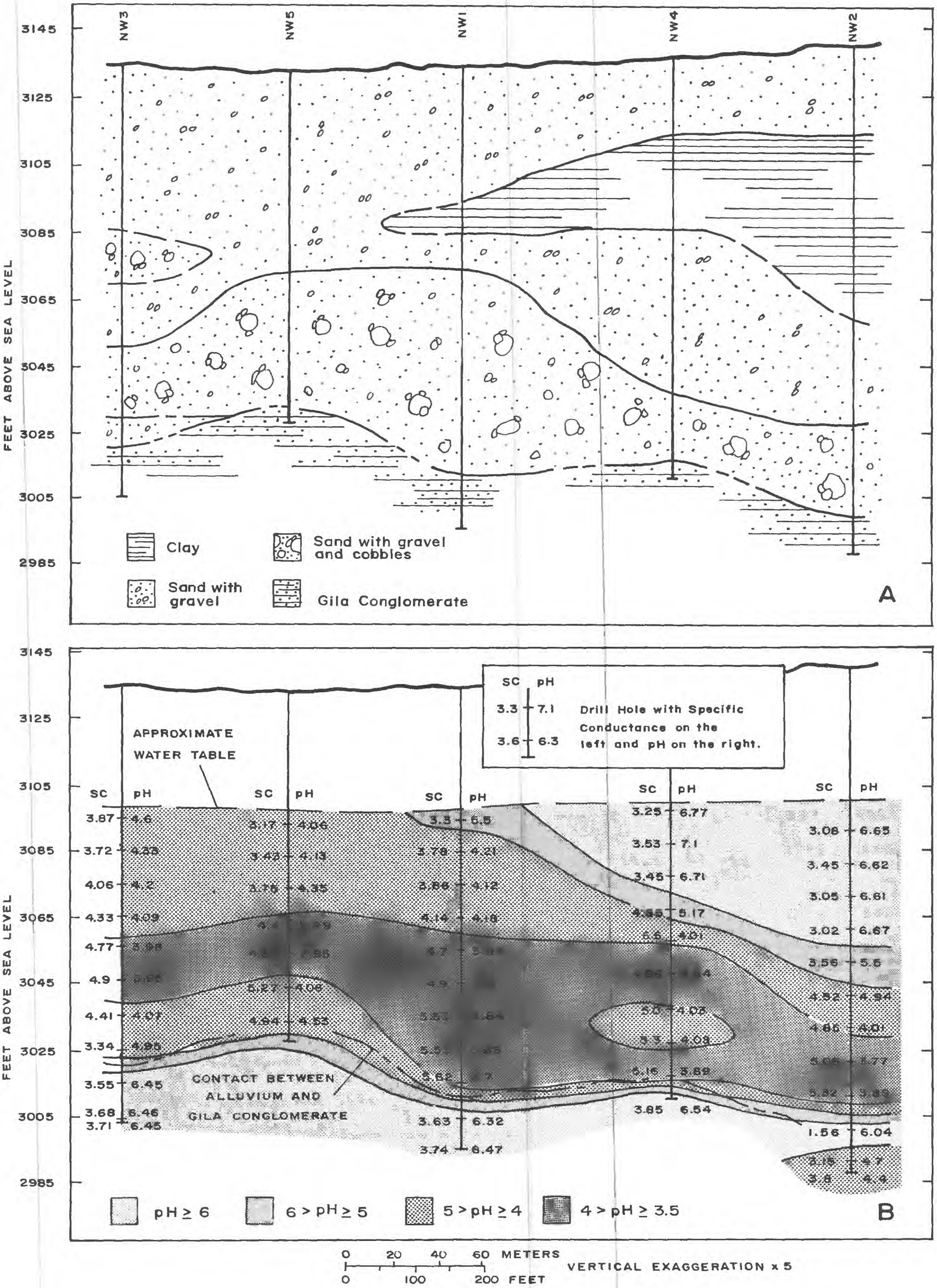
FEET ABOVE SEA LEVEL
3145
3125
3105
3085
3065
3045
3025
3005
2985
NW3
NW5
NW1
NW4
NW2
Clay
Sand with gravel and cobbles
Sand with gravel
Gila Conglomerate
A
SC pH
3.3 7.1
3.6 6.3
Drill Hole with Specific Conductance on the left and pH on the right.
APPROXIMATE WATER TABLE
CONTACT BETWEEN ALLUVIUM AND GILA CONGLOMERATE
3.87 4.6
3.72 4.33
4.06 4.2
4.33 4.09
4.77
4.9
4.41 4.07
3.34 4.95
3.55 6.45
3.68 6.46
3.71 6.45
3.17 4.06
3.43 4.13
3.75 4.35
5.27 4.06
4.64 4.53
3.3 6.5
3.78 4.21
3.86 4.12
4.14 4.18
4.7
4.9
3.63 6.32
3.74 6.47
3.25 6.77
3.53 7.1
3.45 6.71
4.85 5.17
3.85 6.54
3.08 6.65
3.45 6.62
3.05 6.61
3.02 6.67
3.56 5.6
4.52 4.94
4.65 4.01
1.56 6.04
3.15 4.7
3.8 4.4
pH ≥ 6
6 > pH ≥ 5
5 > pH ≥ 4
4 > pH ≥ 3.5
B
0 20 40 60 METERS
0 100 200 FEET
VERTICAL EXAGGERATION x 5

Figure 2. Cross-sections showing lithology and water chemistry at the Nugget Wash wells. Upper: lithologic cross-section, Lower: Variability in pH and specific conductance.

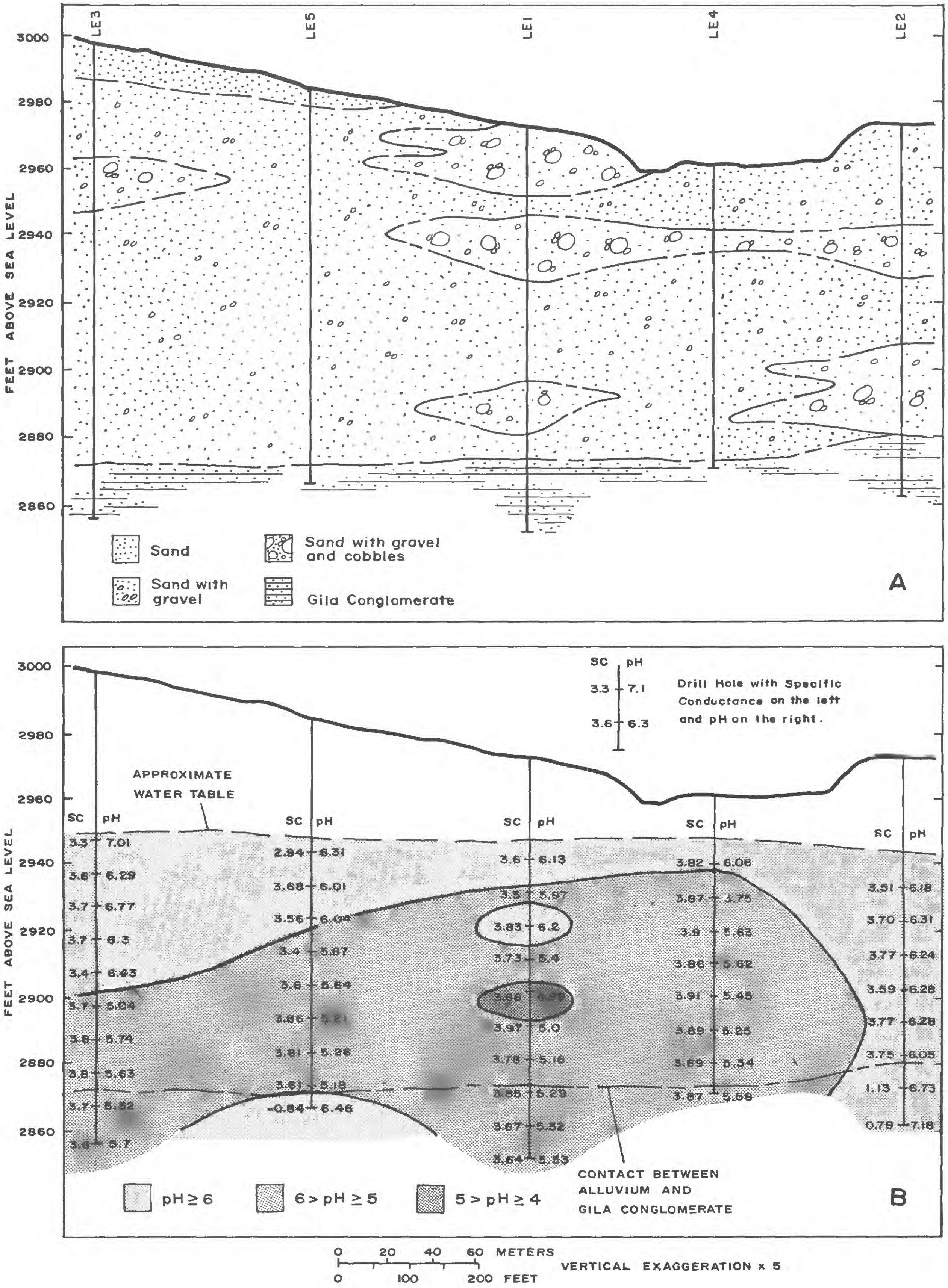
3000
2980
2960
2940
2920
2900
2880
2860
FEET ABOVE SEA LEVEL
LE3
LE5
LE1
LE4
LE2
Sand
Sand with gravel
Sand with gravel and cobbles
Gila Conglomerate
A
SC pH
3.3 7.1
3.6 6.3
Drill Hole with Specific Conductance on the left and pH on the right.
APPROXIMATE WATER TABLE
SC pH
3.3 7.01
3.6 6.29
3.7 6.77
3.7 6.3
3.4 6.43
3.7 5.04
3.8 5.74
3.8 5.63
3.7 5.52
3.6 5.7
2.94 6.31
3.68 6.01
3.56 6.04
3.4 5.87
3.6 5.64
3.86 5.21
3.81 5.26
3.61 5.18
-0.84 6.46
3.6 6.13
3.5 5.97
3.83 6.2
3.73 5.4
3.97 5.0
3.78 5.16
3.85 5.29
3.67 5.32
3.64 5.53
3.82 6.06
3.87 4.75
3.9 5.63
3.86 5.62
3.91 5.45
3.89 5.25
3.69 5.34
3.87 5.58
3.51 6.18
3.70 6.31
3.77 6.24
3.59 6.28
3.77 6.28
3.75 6.05
1.13 6.73
0.79 7.18
pH ≥ 6
6 > pH ≥ 5
5 > pH ≥ 4
CONTACT BETWEEN ALLUVIUM AND GILA CONGLOMERATE
B
0 20 40 60 METERS
0 100 200 FEET
VERTICAL EXAGGERATION x 5

Figure 3. Cross-sections showing lithology and water chemistry of the Leading Edge wells. Upper: lithologic cross-section, Lower: Variability in pH and specific conductance.

AQUIFER RESTORATION UNDER THE CLEAN WATER ACT

By Shirin Tolle[1] *and* Greg V. Arthur[1]

ABSTRACT

The Clean Water Act can be used to cause a responsible party to restore an aquifer if there is proof of a connection between the contaminated ground water and impacted surface waters. The Clean Water Act's advantages are its speed and ease of application.

INTRODUCTION

Aquifer restoration has not been a usual function of the Clean Water Act [33 U.S. Code Section 1251 *et seq.*], which was enacted to protect surface-water quality. However, the surface-water quality of Pinal Creek, near Globe, Ariz., depends on the quality of its underlying aquifer because ground waters surface along its reach. As a result, the U.S. Environmental Protection Agency (USEPA) issued an administrative order under the Clean Water Act in 1987 that required the Inspiration Consolidated Copper Company[2] to keep contamination in the underlying aquifer from surfacing. The Order required Inspiration Consolidated Copper Company to eliminate its sources of aquifer contamination and to remove contamination already in the aquifer. The purpose of this paper is to show when the Clean Water Act can be used to cause the restoration of contaminated aquifers.

PINAL CREEK AQUIFER RESTORATION

In 1981, the Central Arizona Association of Governments documented poor water quality throughout the Pinal Creek watershed (fig. 1) caused by mining (Envirologic Systems, Inc., 1983). In 1985 and 1986, USEPA found that contaminated ground water was surfacing at two main locations and determined that Webster Lake (fig. 1) was by far the largest source of contamination of surface and ground waters in the entire watershed (Arthur, 1987). The Inspiration Consolidated Copper Company formed Webster Lake in the 1940's by damming Webster Gulch (fig. 1) with mining waste and submerging the reach behind the dam with up to 1.4 billion gallons of mining wastewater. Over the years, Webster Lake leaked through the lake bottom into the alluvium of the now-buried Webster Gulch and into the aquifer beneath Miami Wash and Pinal Creek (fig. 1) (Hydro Geo Chem, Inc., 1989).

The 1987 USEPA Order (Docket No. IX-FY86-78) required the Inspiration Consolidated Copper Company to drain Webster Lake. By 1988, the new owner of the mine, Cyprus Mining Company, had drained the lake through consumption of Webster Lake water in milling and leaching processes and through evaporation on tailings piles.

The Order then required mining wastewater already in the underlying aquifer to be removed with withdrawals taken first from the most contaminated parts of the aquifer. In 1987, pumping began from the Kiser subbasin near Miami Wash (fig. 1). Removals were limited by the capacity to consume or evaporate wastewater. After Webster Lake was drained in 1988, intensive pumping began from the buried Webster Gulch channel, and from the Kiser and the Burch subbasins, which lie near the confluence of Miami Wash with Pinal Creek (fig. 1).

Even without fully determining the fate and transport of contaminants in the aquifer, the first steps of any restoration effort would have been the draining of Webster Lake and, the capture of the dirtiest ground waters in old Webster Gulch, and the Kiser and Burch subbasins. As a result, while these actions were ongoing, the Order required the Cyprus Mining Company to characterize aquifer contamination and determine what other actions would be needed to restore the aquifer. By 1989, the Cyprus Mining Company found that the acidic part of the contamination plume would surface in the perennial flow reach of Pinal Creek unless the leading edge of the plume were captured (Hydro Geo Chem, Inc., 1989). As a result, in 1990, intensive withdrawals began from the leading edge at Sunflower Ranch nearly 14 miles downstream from Webster Lake (fig. 1).

A model developed in the aquifer-characterization work predicts a slowed advance of the acidic plume in the aquifer through 1992, a reversal in 1993, and improving aquifer quality after 1993 (Hydro Geo Chem, Inc., 1989). The model predicts that the acidic plume will not surface. As of early 1991, the acidic part of the contamination plume continues to advance but has not surfaced.

USE OF THE CLEAN WATER ACT

In order to cause the restoration of the Pinal Creek aquifer, USEPA used the Clean Water Act because of its speed and ease. The Clean Water Act does not require a great deal of proof nor require the facility to go through a ranking process such as is required with the Comprehensive Environmental Response Compensation and Liability Act "Superfund" [42 U.S. Code Section 9601 *et seq*]. The Clean Water Act requires only proof of a discharge of contaminants from a point source to a water of the United States. In Pinal Creek, the point sources were the seeps of contamination originating from the discharge of Webster Lake mining wastewaters through the underlying aquifer into the surface waters of Pinal Creek and Miami Wash, both of which are defined as waters of the United States.

The Clean Water Act allows USEPA to cause point-source dischargers to cease discharge. It does not specifically give USEPA the capability to enforce remediation at facilities where a discharge to ground water may contaminate surface water. However, USEPA and the U.S. Department of

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[1] U.S. Environmental Protection Agency, San Francisco, Calif.

[2] The use of industry or firm names in this paper is for location purposes only, and does not impute responsibility for any present or potential effects on the natural resources.

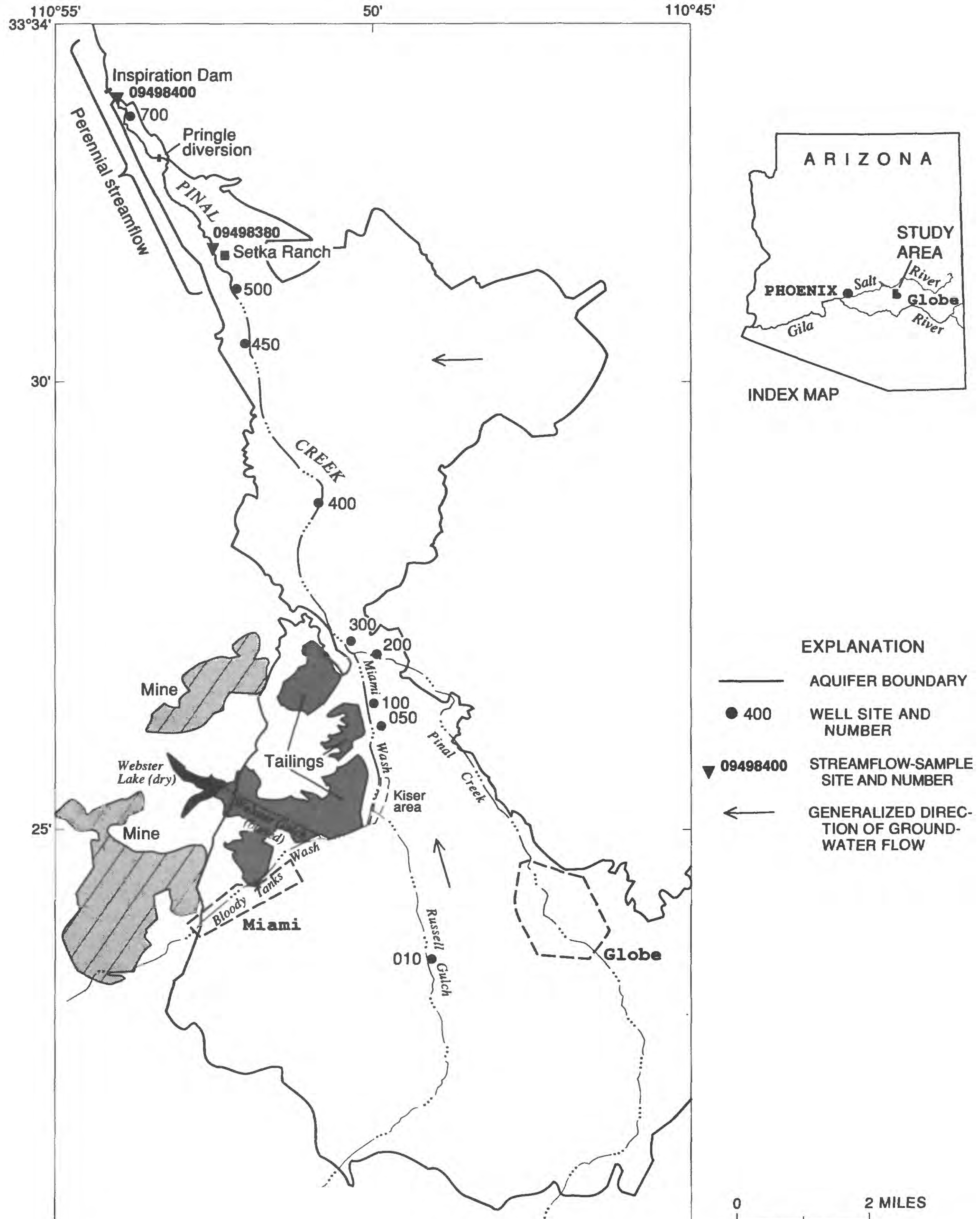
110°55'
50'
110°45'
33°34'
30'
25'
33°20'
Inspiration Dam
09498400
700
Pringle diversion
Perennial streamflow
PINAL
09498380
Setka Ranch
500
450
CREEK
400
300
200
Miami
Wash
100
050
Mine
Tailings
Webster Lake (dry)
Pinal
Creek
Kiser area
Mine
Wash
Bloody
Tanks
Miami
Russell
Gulch
010
Globe
ARIZONA
STUDY AREA
PHOENIX
Salt
River
Globe
Gila
River
INDEX MAP
EXPLANATION
AQUIFER BOUNDARY
● 400 WELL SITE AND NUMBER
▼ 09498400 STREAMFLOW-SAMPLE SITE AND NUMBER
GENERALIZED DIRECTION OF GROUND-WATER FLOW
0
2 MILES
0
2 KILOMETERS

Figure 1. Area of study.

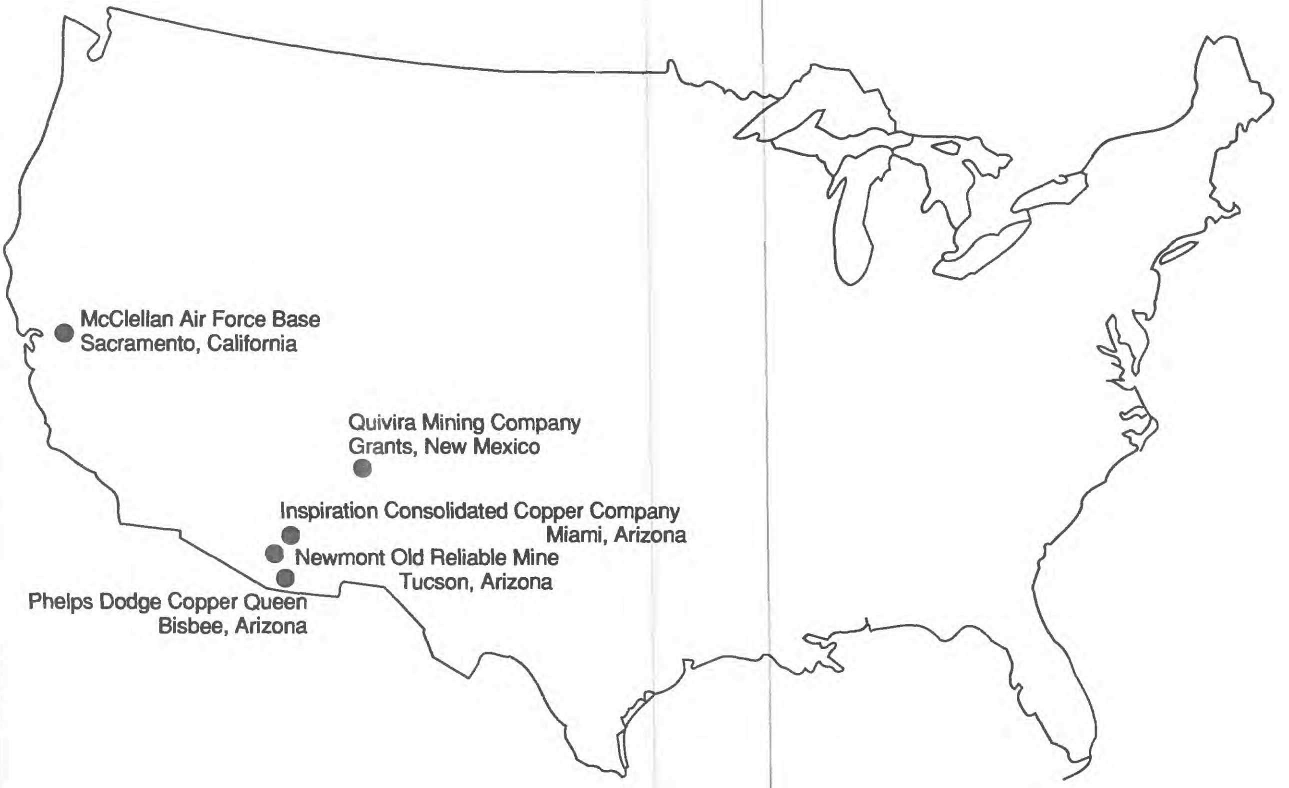

Figure 2. Sites where the Clean Water Act was applied to surfacing ground waters.

Justice have reached a consensus that, if there is a documented nexus (that is, a reasonable proof of a connection between ground water and surface water), USEPA can enforce remediation under the Clean Water Act against a facility whose discharge is to ground water. In a case such as Pinal Creek, the path of ground water through the alluvium is considered a conduit. As a result, a discharge to alluvial ground water that eventually affects surface water remains regulated under the Clean Water Act even though it is not specifically referenced in the law or regulations.

Nevertheless, Federal case law, though inconsistent, has tended to indicate that the Clean Water Act cannot be relied upon to protect ground water (Manning, 1987). In one case, *U.S. v. Quivira Mining Co* 765 F. 2d 126 (1985), the Court of Appeals supported USEPA's finding that two normally dry arroyos near Grants, N. Mex. (fig. 2), are waters of the United States because of surface connections to streams during storms and regular ground water connections into aquifers that surface into the same streams. As a result, the ground to surface-water connection in this case provided at least a partial basis to regulate the discharge of contaminants from the mine to the arroyos under the Clean Water Act.

In another Federal court decision, *McClellan Ecological Seepage Situation (Mess) v. Weinburger*, 655 F. Supp. 601 E.D. Cal. 1986), the District Judge ruled against MESS, an environmental group, in a case involving discharge to ground water from McClellan Air Force Base (fig. 2). MESS claimed that McClellan Air Force Base discharged contaminants into ground water without a permit. The Judge ruled that a discharge to isolated ground water does not require Federal permits but that MESS should have the opportunity to engage in additional discovery to demonstrate that a hydrologic connection exists between the ground water and surface waters that themselves constitute "navigable water." As of early 1991, the MESS group has not been able to prove the connection between ground water and surface water at the site.

However, USEPA has achieved voluntary compliance with Administrative Orders issued under the Clean Water Act where the nexus has been clearly defined. At the Phelps Dodge Copper Queen Mine, near Bisbee, Ariz. (fig. 2), seepages into surface waters were traced from surface impoundments some as far away as 2,000 feet. USEPA established the nexus through the comparison of samples taken from the seeps and impoundments. USEPA's 1985 Order (Docket No. IX-FY86-44) required Phelps Dodge to intercept seepages.

Another similar case of voluntary compliance was achieved at the Newmont Old Reliable Mine, near Tucson, Ariz. (fig. 2). Acid mine drainage from the base of the Old Reliable Mine leach area was identified as a point source in the 1986 Order (Docket No. IX-FY86-80). The Order required Newmont Old Reliable Mine to intercept the acid mine drainage before it reached surface waters.

In the restoration of the Pinal Creek aquifer, Inspiration Consolidated Copper Company and its successor, Cyprus Mining Company, also voluntarily complied with an Administrative Order under the Clean Water Act (Docket

No. IX-FY86-78). Alternative enforcement action taken under the Clean Water Act could have supported an emergency order under Section 431 of the Safe Drinking Water Act [42 U.S. Code Section 300f *et. seq.*] to protect the underground source of drinking water or the case could have been referred for enforcement under the Resource Conservation and Recovery Act [42 U.S. Code Section 6901 *et. seq.*] or Superfund. The Primary Drinking Water Standards also could have been applied because of the potential for contaminated seepage in Pinal Creek to reach Roosevelt Lake, which is a source of drinking water. The severity and extent of the contamination at the site could also have led to ranking the mine on the Superfund National Priorities List. However, enforcement under the Clean Water Act allowed the principal facility to initiate remediation immediately. As more about the contamination became known, USEPA modified the Administrative Order to require specific longer-term actions.

ADVANTGAGES

The use of the Clean Water Act allowed USEPA to require Inspiration Consolidate Copper Company to perform the most obvious remedial actions before the entire problem was characterized and without a determination of what other responsible parties might have contributed to the contamination. As a result, Inspiration Consolidated Copper Company immediately began to eliminate its main source of contamination, Webster Lake, and followed with withdrawals of the most contaminated wastewater in the aquifer. Furthermore, USEPA was able to modify its requirements as Cyprus Mining Company learned more about the contamination. If these actions were delayed 3 years until completion of the characterization study in 1989, the acidic part of the plume might have surfaced in the perennial reach of Pinal Creek by now.

SUMMARY

The Clean Water Act can be used to cause a responsible party to restore an aquifer if there is proof of a connection between the contaminated ground waters and affected surface waters. Because alluvial waters under Pinal Creek surface along its reach, USEPA used the Clean Water Act to cause the Inspiration Consolidated Copper Company and its successor, Cyprus Mining Company to eliminate Webster Lake, which was the main source of contamination to the aquifer. USEPA then required the company to pump out the most contaminated part of the aquifer and to characterize the contamination concurrently. Cyprus Mining Company now also withdraws water from the leading edge of the contamination plume.

In order to establish a violation of the Clean Water Act, USEPA only needs to prove that an owner or operator discharged contaminants from a point source into a surface water. Furthermore, under the Clean Water Act, USEPA can cause a responsible party to cease discharge of pollutants to the surface water (which in the case of Pinal Creek involves restoration of the aquifer) without finding all responsible parties, without ranking the site, and without completing a characterization study of the problem. The Clean Water Act's advantages are its speed and ease of application.

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BENTHIC INSECTS AS INDICATORS OF LARGE-SCALE TRACE METAL CONTAMINATION IN THE CLARK FORK RIVER, MONTANA

By Daniel J. Cain[1] *and* Samuel N. Luoma[1]

ABSTRACT

The Clark Fork River in western Montana has been contaminated with metals by mining in its headwaters over the past 125 years. Metals originally discharged into the river from an upstream source(s) now contaminate bed sediments 550 kilometers downriver. Metal contamination in the benthic invertebrate community was evaluated over a 381 kilometer reach of the upper river. Six benthic insect taxa, including two caddisflies (Trichoptera) and four stoneflies (Plecoptera), were selected for study. Distributions of these taxa differed within the river and only one taxon, Hydropsyche spp., was collected at all stations. Whole-body metal concentrations in all six taxa from the Clark Fork were elevated relative to specimens collected from uncontaminated tributaries. Contamination patterns, however, varied among taxa and metals. Spatial trends in metal concentrations in two closely related caddisflies, Hydropsyche spp. and Arctopsyche grandis, correlated ($p<0.05$) with the downriver decrease in metal concentrations in the sediments, although within the same station, the absolute metal concentrations in Hydropsyche spp. were approximately two times greater than in Arctopsyche grandis. Downriver decreases in the concentrations of some metals also were evident in plecopterans; however, metal concentrations in these animals generally were not significantly correlated with sediment metal concentrations. Differences in metal concentrations among taxa were largely explained by differences in feeding habit. Metal concentrations were higher and showed a stronger relation to sediment metal concentrations in omnivorous filter feeders and detritivores than in predators. The results clearly established the presence of metal contamination in benthic invertebrates throughout the 381-kilometer study reach.

INTRODUCTION

The large-scale extraction and processing of metal-rich ores in watersheds has created extensive contamination of streams and rivers (Moore and Luoma, 1990). Without proper containment, waste material can be transported far downstream from the site of mining activities (Johns and Moore, 1985; Andrews, 1987; Moore and others, 1991). Little is known about the biological fate of trace metals in river systems.

The benthic insect community is an important component of cobble-bottom stream ecosystems, both in terms of its productivity and its role in the aquatic food web. Benthic insects accumulate trace metals in response to elevated metal exposures (Nehring, 1976; Spehar and others, 1978; Besser and Rabeni, 1987), and have been used to assess the availability of metal contaminants to aquatic animals (Burrows and Whitton, 1983; Lynch and others, 1988; Moore and others, 1991; Axtmann and others, in press).

In this paper metal contamination in benthic insects is examined over a 381-km (kilometer) reach of the Clark Fork River, Mont. The downriver distributions of copper (Cu), cadmium (Cd), lead (Pb), and zinc (Zn) concentrations in benthic insects are compared with metal concentrations in fine-grained bed sediments of the Clark Fork River, Mont. Variables affecting species-specific differences in whole-body metal concentrations are addressed. The effectiveness of benthic insects as bioindicators of metal contamination also is discussed.

MATERIALS AND METHODS

Site Description

The city of Butte is located at the headwaters of the Clark Fork River in western Montana. Discharge of tailings material into Silver Bow Creek and Warm Springs Creek from mining operations in and around Butte led to extensive metal contamination of sediments and biota in the Clark Fork (Andrews, 1987; Moore and Luoma, 1990; Axtmann and Luoma, 1991; Axtmann and others, in press). Cu was the primary metal mined although other metals including Pb and Zn were extracted (Perry, 1932). Metal contamination in bed sediments decreases with distance downriver and presently extends at least 550 km below the original site of discharge (Johns and Moore, 1985; Axtmann and Luoma, 1991).

Sample Collection and Analyses

Based upon the findings of a reconnaissance in August 1985, the larvae or nymphs of six taxa of benthic insects were targeted for collection in 1986. The taxa included two caddisflies (Trichoptera), *Hydropsyche* spp. and *Arctopsyche grandis*, and four stoneflies (Plecoptera), *Claassenia sabulosa*, *Hesperoperla pacifica*, *Isogeniodes* sp., and *Pteronarcys califorica*. These taxa were chosen because (1) they were abundant at many stations, and the individuals of each taxon were relatively large which ensured sufficient biomass for trace-metal analysis; (2) they had direct or indirect contact with sediments; and (3) they represented different trophic levels. In August 1986, samples were collected with kick nets from riffle areas at 15 stations in the upper 381 km of the Clark Fork River (all distances measured as kilometers downstream from the confluence of Warm Springs Creek) (fig. 1). Metal concentrations in Clark Fork insects were referenced against the average metal concentrations in insects collected in August 1986, April 1987, June 1987, August 1987, and August 1989 from two tributaries, Rock Creek and the Blackfoot River.

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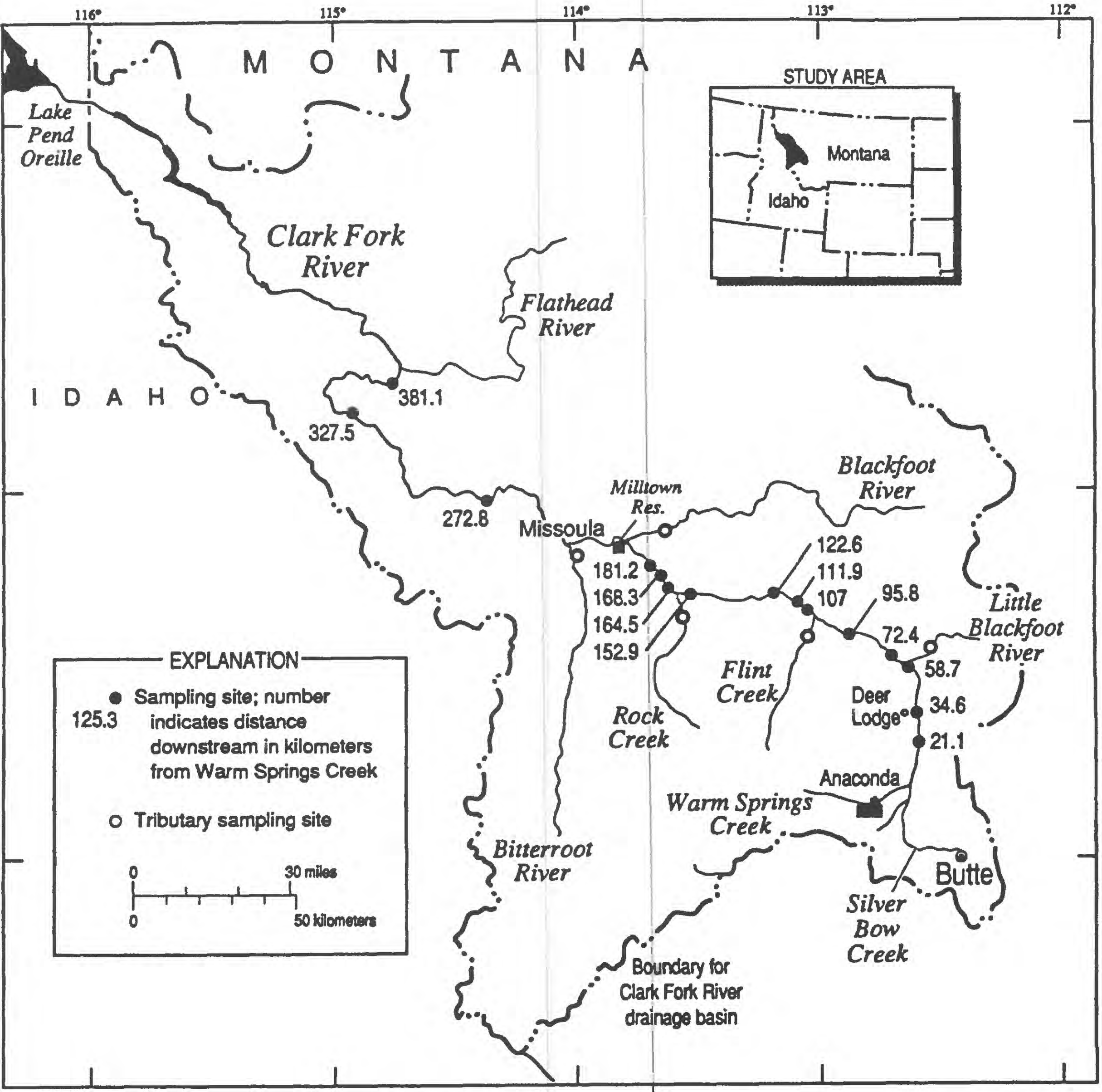
116°
115°
114°
113°
112°
48°
47°
46°
M O N T A N A
I D A H O
Lake Pend Oreille
Clark Fork River
Flathead River
381.1
327.5
272.8
Missoula
Milltown Res.
Blackfoot River
122.6
111.9
107
95.8
181.2
168.3
164.5
152.9
72.4
58.7
34.6
21.1
Little Blackfoot River
Flint Creek
Rock Creek
Deer Lodge
Anaconda
Warm Springs Creek
Butte
Silver Bow Creek
Bitterroot River
Boundary for Clark Fork River drainage basin
STUDY AREA
Montana
Idaho
EXPLANATION
● Sampling site; number 125.3 indicates distance downstream in kilometers from Warm Springs Creek
○ Tributary sampling site
0
30 miles
0
50 kilometers

Figure 1. Map of the Clark Fork River showing station locations.

Reference samples were collected within 25 km of the confluences of the Clark Fork. Sampling of the major tributaries in the watershed indicated that sediment metal concentrations in these two tributaties were representative of regional pre mining conditions (Axtmann and Luoma, 1991). Specimens were sorted on site by taxon, then held in plastic bags filled with ambient riverwater in an ice cooler for 4 to 6 hours to provide the insects an opportunity to clear their digestive tracts. The water in the bags was then drained and the insects were frozen. Samples were thawed in the laboratory and rinsed with deionized water to remove sediment from the exoskeleton. Identifications of specimens were verified and then individuals from the same taxonomic group were sorted by size to examine possible size-related differences in metal concentrations. Individuals of the same taxon and of similar size were composited into samples to attain a minimum total dry weight of 50 milligrams. Samples were dried at 80 °C, weighed, and then digested by hot 16 N HNO_3 reflux. After the sample solution turned clear, the acid was evaporated and then the residue was reconstituted in 3 N HCl. Metals were determined by flame atomic-absorption spectophotometry (AAS). The quality of the data was checked by analyzing a biological standard (NIST standard reference material 1577a, bovine liver). Concentrations of Cu, Cd, and Zn determined in standards were within the 95 percent confidence intervals of the certified mean concentrations. The reliability of the method could not be verified for Pb because concentrations in the NIST reference material fell below analytical detection limits.

Metal concentrations in insects were correlated with sediment metal concentrations. Fine-grained (<60 micrometer) bed sediments were collected simultaneously with the insect samples. Sediments were sampled, prepared, extracted with 0.6 N HCl, and analyzed by flame AAS as previously described (Luoma and Bryan, 1981, 1982; Axtmann and Luoma, 1991;). Concentration data were normalized by log transformation for the correlation analysis. Statistical significance of a correlation (product-moment correlation coefficient, r) was set at $p < 0.05$.

The effects of feeding habit and size on insect metal concentrations were examined on a subset of data by analysis of covariance. The analysis included a subset of data from four stations located between 60 and 181 km where all six taxa were present. The insects were separated into three feeding categories: detritivore, omnivore (filter-feeders), and predator. Feeding habit was the main factor, and the mean dry weight of individuals (size) in each sample was a covariate. The concentration of metals extracted in 0.6 N HCl from bed sediments was included as a covariate to adjust insect concentrations for differences in metal contamination among stations. Metal concentrations were log-transformed for the analysis. Interactions between the main factor and the covariates were examined.

RESULTS AND DISCUSSION

Distribution of Taxa

The availability of the target taxa varied among stations. In the upper 60 km where streamflow was lowest and contamination was greatest fewer taxa were present and their densities were lower than downriver (McGuire, 1988; 1989). Only two of the targeted taxa, *Hydropsyche* spp. and *Isogenoides* sp., were collected for a metals sample. All six taxa were collected between 61 and 191 km, but farther downstream *Isogenoides* sp., *Pteronarcys californica*, and *Hesperoperla pacifica* were not available in sufficient - quantities for trace metals samples. *Hydropsyche* spp. was the only taxon distributed throughout the 381-km study reach.

Metal Contamination in Insects

Metal concentations in all insect taxa collected in the Clark Fork were higher than concentrations in specimens collected from the reference tributaries. For example, Cu in four taxa are shown in figures 2 and 3. The highest metal-body burdens were in taxa collected in the upper 60 to 181 km where sediments also were the most contaminated. Contamination was evident in the lower 200-km reach. In *Hydropsche* spp., the means of the Cu and Cd concentrations of the three most downriver stations (270-381 km) were significantly greater ($p < 0.05$; t-test) than reference concentrations.

Although contamination was detected in all taxa, the downstream distributions of metals in the insects differed among taxa and metals, and were generally more complex than the exponential decrease in sediment metal concentrations shown by Axtmann and Luoma (1991). Metal concentrations in the trichopterans, *Hydropsyche* spp. and *Arctopsyche grandis*, correlated positively with sediment metal concentrations (table 1), although in some reaches departures from the overall correlations were evident. For example, between 20 and 100 km below the Warm Springs Ponds, Cd in *Hydropsyche* spp. increased as sediment Cd concentrations decreased significantly. In the plecopterans, downstream decreases were detected in Cd and Cu in *Isogeniodes* sp., and in Cd in *Claassenia sabulosa*. Concentrations of Cu (fig. 3), Cd, and Pb also decreased downstream in the detritivore *Pteronarcys californica*, but they did not correlate significantly with sediment concentrations possibly because of the small sample size.

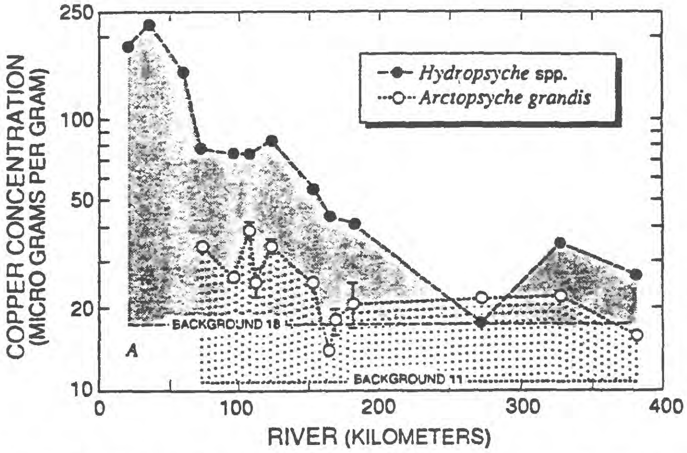

Figure 2. Copper concentrations in *Hydropsyche* spp. and *Arctopsyche grandis* (Trichoptera) in the Clark Fork. Background concentrations are the mean concentration of speciments of each taxon collected from uncontaminated tributaries.

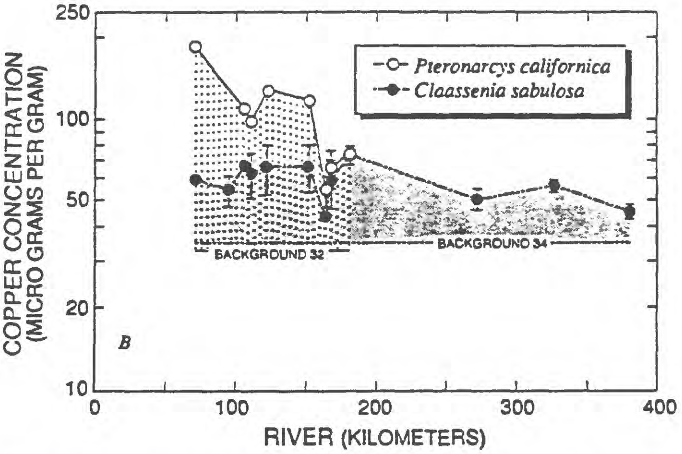

Figure 3. Copper concentrations in *Pteronarcys californica* and *Claassenia sabulosa* (Plecoptera) in the Clark Fork. Background concentrations are the mean concentration of speciments of each taxon collected from uncontaminated tributaries.

Table 1. *Correlation of whole-body insect metal concentrations and bed sediment metal concentrations. Correlation coefficients, r, and sample sizes (in parentheses) are shown*

Taxon	Copper	Cadmium	Lead	Zinc
Trichoptera				
Hydropsyche spp.	0.86(13)[1]	0.71(13)[2]	0.74(13)[2]	.74(13)[2]
Arctopsyche grandis	.63(12)[3]	.84(12)[1]	.61(12)[3]	.69(12)[3]
Plecoptera				
Claassenia sabulosa	.53(12)	.69(12)[3]	.26(12)	.53(12)
Hesperoperla pacifica	.00(7)	- .63(7)	.69(5)	.43(7)
Isogenoides sp.	.74(12)[2]	.66(12)[3]	.36(11)	.25(12)
Pteronarcys californica	.68(8)	.51(8)	.66(8)	.37(8)

[1] p <0.001
[2] p <0.01
[3] p <0.05

Effects of Feeding Habit and Size

Significant differences in metal concentrations were found among taxa. Analysis of covariance indicated that these difference could be explained by differences in the feeding habits of the insects. Within the 60 to 181 km reach, concentrations of Cu (for example, compare figs. 2 and 3) and Pb were highest in the detritivore, *Pteronarcys californica*. Concentrations of Pb were intermediate in omnivores such as *Hydropsyche* spp., and lowest in the predators. Cd concentrations were slightly higher in the omnivores, and Zn concentrations were highest in the three predaceous stoneflies (although the mean Zn concentration in the predators was greatly influenced by one species, *Hesperoperla pacifica*). Similar findings have been reported by others. Burrows and Whitton (1983) reported lower concentrations of Cu, Pb, and Zn in predators than in phytophagous species. Smock (1983b) showed that the whole-body concentrations of cobalt, chromium, iron, antimony, and scandium were higher in taxa that ingested sediments than in predators and that these patterns were influenced by contaminant burdens of material contained in the guts of the animals (Smock, 1983b). These results suggest that the Clark Fork insects had not evacuated their guts prior to analysis.

Differences in the average dry weights of specimens of the same taxon ranged from twofold to sixfold. Among taxa, differences in dry weight exceeded an order of magnitude. Metal concentrations either within or among taxa did not display any consistent relation with dry weight (size). Analysis of covariance did not detect any significant effect of dry weight on metal concentrations except for an interaction between metal concentrations and dry weight in the filter-feeding group. This appeared to be due to differences in metal concentrations between *Hydropsyche* spp. and *Arctopsyche grandis*. Concentrations of Cu (fig. 2) and Pb in the smaller *Hydropsyche* spp. were typically two times greater than in *A. grandis*. These differences could be due to surface contamination. They also may reflect relative differences in the compositions of the animals' diets. *Arctopsyche grandis* is more predaceous than *Hydropsyche* spp. (Wiggins, 1977).

Insects as Bioindicators

The results of this study illustrate some of the benefits and challenges in the employment of benthic insects as indicators of large-scale geochemical contamination. Benthic insects are widely dispersed in river systems, and they can be collected with simple methods. Individual sizes of organisms are relatively small, but, in many locations, densities are great enough to ensure sufficient biomass to meet analytical detection limits. Relative metal concentrations in the bodies of insects can be used to detect contamination (Burrows and Whitton, 1983; Besser and Rabeni, 1987; Hatakeyama and others, 1988; Lynch and others, 1988; Moore and others, 1990). Collectively, the metal concentrations in six taxa clearly established the presence of contamination throughout a 381-km study reach of the Clark Fork River. Direct comparisions of metal contamination over large distances, however, can be handicapped by changes in the species composition of the benthic community. In lieu of a single cosmopolitan species, interpretations of contaminant distributions may rely on closely related taxa whose ranges overlap. *Hydropsyche* spp. is a widely distributed taxon in cobble-bottom rivers and appears to tolerate high metal concentrations. Therefore, this taxon may be a good candidate for a bioindicator in this habitat. Most studies of trace metals in insects report whole-body concentrations. Legitmate concerns have been raised about the reliability of these data for assessments of metal bioavailability and toxicity because they include metals associated with the contents of the gut or adsorbed to external surfaces (Elwood and others, 1976; Smock, 1983a,b; Krantzberg and Stokes, 1988; Cain and others, 1989; Hare and others, 1989). Metal concentrations in taxa from the Clark Fork generally did not exhibit any consistent relation to size, indicating that the quantity of metals sorbed to the exoskeleton was small relative to metals absorbed into soft tissues and associated with material in the gut. Gut contamination can be reduced by depurating animals after they are collected (Hare and others, 1989). However, the procedure used in this study to clear the contents of the insects' guts apparently was ineffective. The differences in metal concentrations detected among feeding groups suggested that the gut content was a significant source of contamination. The influence of the gut content on whole-body concentrations was examined further. The high concentrations of Cu and Pb in the detritivore *Pteronarcys californica* combined with the large volume the species' gut suggested that gut contamination was greatest in this taxon. In August 1989, *Pteronarcys californica* were collected from one contaminated station in the Clark Fork (river km 168) and two tributaries (Flint Creek and Rock Creek) following the procedures used in 1986. The gut and the body (minus the gut) of these specimens were dissected and analyzed separately. Whole-body concentrations were reconstructed from these analyses. Depending on the element, the body contained 40 to 80 percent of the total burden of Cd, Cu, Pb, and Zn (Axtmann and others, in press). Both the body excluding the gut and the whole body reflected the relative differences in sediment metal contamination among the three stations. The differences in whole-body metal concentrations, therefore, were not simply due to gut contamination, but indicated relative differences in metal availability. Clearly, more work is needed to define the relation between whole-body metal burdens and metal bioavailability. This is a critical step in linking environmental metal contamination to toxic effects on the aquatic invertebrate community.

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ISOLATION OF MULTIPLE CLASSES OF PESTICIDES FROM LARGE-VOLUME WATER SAMPLES USING SOLID PHASE EXTRACTION CARTRIDGES

By William T. Foreman[1] and Gregory D. Foster[2]

ABSTRACT

A solid-sorbent sampling method that provides for the trace enrichment of multiple chemical classes of organic pesticides is described. High-capacity solid-phase extraction cartridges containing 10 grams of octadecylsilyl-bonded porous silica were evaluated for their ability to preconcentrate 38 pesticides spiked into 10 Liters of distilled water. Single cartridge collection efficiencies were very good for nearly all pesticides evaluated, except for dimethoate, a polar, highly water-soluble compound. Retention of analytes by the front cartridge alone accounted for an average 71 to 102 percent recovery of the total mass of analyte spiked for all but three analytes. For studies in which low sample flow rates of 20 to 35 milliliters per minute can be used to extract 10 liters of water, high-capacity solid-phase extraction appears suitable for the isolation and preconcentration of a variety of pesticide classes.

INTRODUCTION

Mass-balance methods used to investigate and model the environmental transport and fate of organic contaminants rely largely on the ability to establish the distribution of (detect) the contaminant in the relevant environmental compartments (matrices). Adjustment of analyte enrichment factors is often used to vary the detection limit of the method, and is typically accomplished by adjusting the sample volume and(or) the final extract volume before instrumental analysis. Numerous conventional analysis methods for trace organic contaminants in water use 1-L (liter) water samples extracted by separatory funnel liquid-liquid extraction (see, for example, Wershaw and others, 1987; U.S. Environmental Protection Agency, 1988). However, for ultra-trace level contaminant analysis, extraction of larger sample sizes is desired to enhance enrichment of the contaminant and, hopefully, lower detection limits.

Several investigations have been undertaken in this laboratory exploring alternative methods for isolating and preconcentrating trace organic pesticides from volumes of water larger than 1 L in an effort to obtain lower detection limits. In one approach, the Goulden[3] large sample extractor --a continuous flow liquid-liquid extractor--was utilized to isolate pesticides from 10- to 100-L water samples (Foster and Rogerson, 1990; Foster and others, 1991).

An alternative to liquid-liquid extraction being investigated is the use of solid-phase sorbents to preconcentrate trace organic contaminants from filtered water samples--an approach termed "solid phase extraction[4] (SPE) (or liquid-solid extraction). Although a variety of solid-sorbent materials have been used to preconcentrate organics from water, application of the bonded phase silica sorbents has expanded rapidly (Zief and Kiser, 1990). Over the past decade, a number of investigators have used cartridges containing 100 mg (milligrams) to 1 g (gram) of the reverse-phase-type bonded phase silica sorbents, such as octadecylsilyl-silica (C-18) to isolate organics from ≤ 1-L volumes of water (see for example, Renberg and Lindstrom, 1981; Andrews and Good, 1982; Junk and Richard, 1988; Kicinski and others, 1989; Ritsema and others, 1989; Vinuesa and others, 1989; Durhan and others, 1990) up to 4 L of seawater (Hinckley and Bidleman, 1989). The recent introduction of disposable cartridges containing 5 g and 10 g of C-18 packing has provided an opportunity to apply this SPE approach to volumes of water larger than 4 L, an application not previously reported.

An investigation of the use of 10-g C-18 sorbent cartridges to isolate a variety of pesticides from 10-L water samples has been undertaken. The objectives of the entire SPE project are to (1) determine the spike recoveries in distilled and natural waters of a broad suite of pesticides differing in physicochemical properties, (2) determine analyte collection efficiency on the cartridges, and (3) compare extraction performance, replication, and limits of detection achieved in the preconcentration of pesticides using the SPE cartridges to identical extractions carried out using the Goulden large sample extractor. This paper describes the method experimental procedure, along with results of distilled water spike recoveries and cartridge collection efficiencies.

METHODS

Target pesticides, obtained in neat form from the U.S. Environmental Protection Agency's Pesticides and Industrial Chemicals Repository (Research Triangle Park, N.C.), were used as received to prepare a mixed-pesticide spike solution in methanol at a concentration of approximately 10 ng/mL (nanograms per milliliter) for each. All solvents were residue grade from Burdick and Jackson (Muskegon, Mich.).

A 10-L volume of distilled water, contained in a 40-L milk can, was spiked with 100 mL (milliliters) of the mixed-spike solution containing the 38 pesticides listed in table 1; the final concentration of each was approximately 100 nanograms per liter. The methanol carrier (100 mL) represented 1 percent of the sample volume and was included to help maintain sorbent activation during sample processing (see DISCUSSION). The water sample was mixed and allowed to equilibrate for 1 hour before sample isolation.

The disposable sorbent cartridges contained 10 g of octadecyl-silyl silica (40 micrometer nominal diameter) packed into a 60-mL polypropylene housing and held in place with polyethylene frits (Analytichem International, Inc., Harbor City, Calif.). The cartridges were precleaned by passing 60 mL of cyclohexane and isopropanol sequentially through the cartridge under aspiration. The cartridges were conditioned immediately prior to sample isolation by passing 50 mL methanol followed by 50 mL distilled water through the cartridges. At no time were the cartridges allowed to dry following conditioning.

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[3] The use of brand, firm, or trade names in this paper is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

[4] A completely different definition of "solid phase extraction" is the solvent extraction of solid matrices, such as rocks, soil, or sediment.

Two cartridges were connected in tandem (labeled FRONT and BACK in fig. 1) to the sample isolation system, which also consisted of a positive-displacement pump (Model QSY-2 CKC, Fluid Metering Inc., Oyster Bay, N.Y.) with ceramic head, and 1/8 inch polytetrafluorethylene (PTFE) tubing and fittings. The 10-L spiked distilled-water samples were pumped through the cartridges at a rate of 30 to 35 milliliters per minute. The milk can was rinsed with 100 mL of water, which also was pumped through the cartridges. The wastewater generated was not processed further. The cartridges were removed, and interstitial water was displaced by passing dry nitrogen gas through each cartridge for 20 minutes at 15 pounds per square inch, both prior to and following centrifugation of the cartridges at 3,600 rpm (revolutions per minute) for 20 minutes. Each cartridge was separately eluted with 60 mL of 70 percent cyclohexane-isopropanol. The eluant volume was reduced to approximately 5 mL by rotory-flash evaporation, with additional cyclohexane or 70 percent cyclohexane-isopropanol added to the extract until residual water had been completely removed as a three-phase azeotrope. The extract was transferred to a volume-calibrated centrifuge tube, reduced to 0.5 mL by nitrogen blowdown, centrifuged at 2,500 rpm for 10 minutes to draw down residual particles, and transferred to an autosampler vial. Four replicate spike recovery tests were conducted.

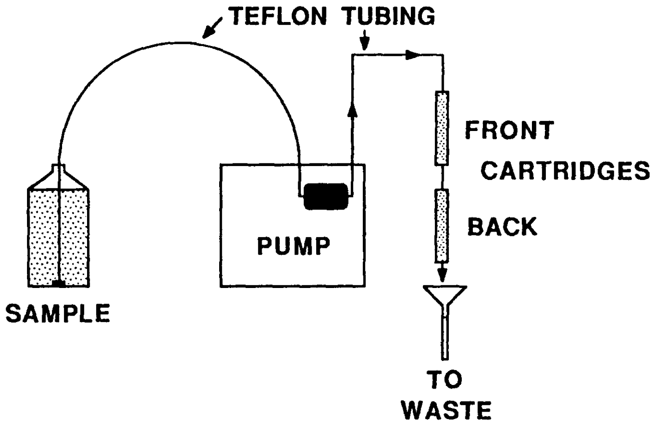

Figure 1. Sample isolation system (not to scale).

The milk cans were rinsed with two 100-mL portions of dichloromethane (called "can rinse"). The dichloromethane was dried with anhydrous sodium sulfate, and reduced to 0.5 mL and solvent exchanged to 70 percent cyclohexane-isopropanol by a combination of rotory-flash and nitrogen evaporation. The rinse was then transfered to an autosampler vial.

An internal injection standard consisting of five perdueterated polycyclic aromatic hydrocarbons was added to each extract vial to give a final concentration of 0.4 nanograms per microliter per component. The extracts were analyzed by gas chromatography-mass spectrometry (GC-MS) under conditions previously described (Foster and Rogerson, 1990; Foster and others, 1991). Quantitation was accomplished by use of internal injection standard calibrations.

RESULTS AND DISCUSSION

The C-18 sorbent reportedly requires preconditioning with a polar water-miscible solvent, such as methanol, to solvate (activate) the sorbent (Van Horne, 1985); otherwise, the hydrophobic octadecylsilyl group will not effectively retain many analytes dissolved in highly polar water. Additionally, 1 percent methanol was added to the 10-L water samples to help maintain sorbent activity during the lengthy sample-processing step. The sorbent-activation step represents a potential difficulty in the widespread field application of this SPE method because of the generation of solvent-tainted wastewater requiring disposal. The development of new-generation sorbents that do not require solvent activation hopefully will eliminate this problem.

The combined nitrogen gas and centrifugation cartridge-drying step was unable to remove all interstitial water from the collection cartridge, resulting in the undesirable need for additional solvent usage during rotory-flash evaporation to achieve water removal with a three-phase cyclohexane/isopropanol/water azeotrope. In a separate project, we recently established that substitution of carbon dioxide for nitrogen provides acceptable drying of 500-mg and 1-g cartridges, and we are planning to evaluate the use of carbon dioxide for drying 10-g cartridges.

Solid-sorbent samplers function as frontal chromatographic systems, because the analyte is continuously introduced to the top of the front cartridge during sample collection and migrates through the sorbent by successive partitioning between the solid-sorbent packing and the water passing through the cartridges. Although more rigorous laboratory experimental approaches exist, a common method for evaluating the collection efficiency of a solid sorbent system under field conditions is to use a tandem-cartridge setup, as applied here (fig. 1), and to analyze the front and back cartridges separately to look for breakthrough of analyte to the back cartridge. This provides an opportunity to measure analyte retention on the cartridges (or, conversely, analyte breakthrough) by comparing the mass of analyte found on the back cartridge relative to that collected on the front trap by the relation

$$\%\ \text{breakthrough} = \left(\frac{\text{mass on back cartridge}}{\text{mass on FRONT cartridge}}\right) \times 100 \qquad (1)$$

When the breakthrough value (in percent) obtained is zero (or very close to zero), the back trap contains either none or much less analyte than the front cartridge, and the analyte is considered completely (or largely) retained on the front cartridge. As the amount of analyte on both traps become similar, it is apparent that some of the analyte has passed through both traps. Typically, when the breakthrough value is <50 percent, analyte collection by both cartridges is considered complete at the volume of sample processed. However, if breakthrough exceeds 50 percent, it becomes more likely that some of the analyte has passed completely through the back cartridge, and analyte collection efficiency is considered poor at that volume of processed sample. Once breakthrough information is known, sample volumes processed can be adjusted to levels well below the volume that gives a 50 percent breakthrough to ensure complete collection of the target compound(s) by the sampling system.

Table 1 presents breakthrough data calculated using equation 1 for the distilled-water spike-recovery experiments. Also shown are the number of experiments (out of four total) where analyte breakthrough to the back trap was detected. Except for dimethoate, which had a 96 percent breakthrough, all analytes were completely retained on two cartridges as indicated by the breakthrough values being well below 50 percent. In addition, 31 analytes were completely collected on the front cartridge as indicated by no detection of the analytes on the back cartridge (no apparent breakthrough). This suggests that only one 10 g cartridge may be necessary for isolation of these 31 analytes from natural waters, assuming no other matrix effects.

Table 1. *Mean analyte recovery and cartridge breakthrough data for four replicate 10-liter spiked distilled-water samples processed by the solid-phase extraction method*

[RSD, relative standard deviation; n, number of breakthrough observations out of four total.]

	Mean percent recovery (percent RSD) for four replicates						Mean percent breakthrough[2]	
	Front cartridge		Can rinse		Total = front + back + rinse[1]			
Organochlorines								
Aldrin	71	(8.8)			71	(8.8)		
4,4'-DDD	94	(2.4)	2.7	(21)	97	(2.9)		
4,4'-DDE	82	(3.6)	5.7	(20)	88	(4.2)		
4,4'-DDT	73	(7.5)	12	(2.7)	97	(2.3)	14	(n=4)
Dieldrin	92	(2.3)			92	(2.3)		
Endrin	95	(6.2)			95	(6.2)		
Endosulfan I	92	(2.1)			92	(2.1)		
Endosulfan II	97	(9.7)			97	(9.7)		
delta-HCH	96	(1.7)			96	(1.7)		
gamma-HCH (Lindane)	91	(2.8)			91	(2.8)		
cis & trans-Permethrin	75	(3.9)	15	(14)	91	(1.4)	0.2	(n=2)
Organophosphates								
Chlorpyrifos	89	(3.8)			89	(3.8)		
Demeton-S	83	(2.5)			83	(2.5)		
Diazinon	95	(1.3)	2.2	(12)	97	(1.5)		
Dimethoate	42	(3.7)			83	(4.6)	96	(n=4)
Disulfuton	80	(2.0)			81	(2.1)	3.1	(n=1)
Ethion	86	(1.4)	14	(1.8)	100	(0.6)		
Malathion	102	(0.9)			102	(0.9)		
Methidathion	92	(1.0)			92	(1.0)		
Methyl parathion	85	(3.9)			85	(3.9)		
Parathion	87	(3.8)			87	(3.8)		
Triazines								
Atrazine	93	(3.3)			93	(3.3)		
Cyanazine	86	(3.2)			86	(3.2)		
Metribuzin	53	(18)			57	(17)	16	(n=2)
Prometon	78	(12)			78	(12)		
Prometryn	92	(5.9)			92	(5.9)		
Simazine	92	(3.4)			92	(3.4)		
Terbuthylazine	95	(2.9)			95	(2.9)		
Chloroacetanilides								
Alachlor	95	(3.3)			95	(3.3)		
Butachlor	96	(2.3)	8.8	(4.3)	105	(8.8)	8.4	(n=1)
Metolachlor	93	(3.6)			93	(3.6)		
Propachlor	100	(3.8)			100	(3.8)		
Thiocarbamates								
Butylate	88	(4.4)			88	(4.4)		
EPTC	78	(4.4)			78	(4.4)		
Miscellaneous								
Linuron	59	(6.0)			59	(6.0)		
Propargite I & II	102	(5.7)	9.0	(15)	113	(3.1)	7.7	(n=1)
Trifluralin	80	(4.7)	12	(0.8)	91	(3.8)		

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[1] Calculated by averaging the total recovery (= recoveries from front cartridge + back cartridge + can rinse) for the four spike recovery tests.

[2] Percent breakthrough = (mass on BACK cartridge/mass on FRONT cartridge) x 100. (See discussion of eq. 1). No entry represents no observations of breakthrough for that analyte in the four replicates.

Breakthrough was observed in all four experiments for 4,4'-DDT and dimethoate. Five other analytes exhibited breakthrough in only one or two tests. The complete dimethoate breakthrough to the back trap is related to its very high water solubility--the highest of the analytes tested. Substantial reduction in the sample volume processed may lower the breakthrough enough to obtain quantitative collection of dimethoate on two 10-g C-18 cartridges. However, a preferred approach for dimethoate collection would be the use of an alternative sorbent material that exhibits far greater retention for this pesticide.

Residues of nine pesticides were detected in the milk-can solvent rinse, and several, like the DDT family, have very low water solubilities. However, others, like diazinon and butachlor, have solubilities 2 to 3 orders of magnitude higher, and their apparent sorption to the can walls was surprising. Solvent rinsing of the sample reservoir (the milk can), appears to be a necessary step to ensure complete quantification, especially for hydrophobic compounds, and possibly could be incorporated as part of the cartridge elution step.

Total analyte recoveries (as a percentage of the amount of pesticide spiked) were calculated by summing the recoveries observed on the front and back cartridges, plus the can rinse for each of the four experiments. The mean and relative standard deviation (as percentages) of the four total recoveries are shown in table 1. For 25 analytes, the mean total recovery was the same as the front cartridge mean recovery inasmuch as the analyte was only detected on the front trap (no breakthrough and no sorption to the milk can occurred). All the analytes had mean total recoveries >78 percent , except for aldrin (71 percent), linuron (59 percent), and metribuzin (61 percent). Because no breakthrough was observed for aldrin and linuron, the lower recoveries for these two compounds may be due to analytical losses during sample workup, incomplete elution from the front cartridge, and(or) compound degradation. The same is likely true for metribuzin, because its average breakthrough was only 16 percent for two of the four recovery experiments, indicating complete collection. The average total recovery for dimethoate was 82 percent, but, considering its large breakthrough (96 percent), the remaining 18 percent may have been lost in the effluent, which was not analyzed. Substantially lower sample volumes are required to ensure complete collection of dimethoate on two 10-g C-18 cartridges.

Although application of tandem-cartridge systems during field sampling of natural water samples is useful as an indicator of breakthrough, it is not a true mass-balance experiment, because the quantity of solute entering the collector is not known except by analysis of the sorbent traps. Also, tandem-trap systems give no indication of analyte losses unrelated to breakthrough, including, for example, compound degradation during sample processing. The use of field-matrix spike samples allows for a more complete assessment of matrix effects on collection efficiency and method performance.

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CHEMICAL MODELING OF ACID MINE WATERS IN THE WESTERN UNITED STATES

By Darrell Kirk Nordstrom[1]

ABSTRACT

Inverse and forward chemical modeling can be applied to the interpretation of mine waste contamination problems with some success. Forward modeling has been used at Iron Mountain, California, to simulate an acid mine water of pH 0.46 based on inverse modeling results. Modeling of such concentrated acidic mine waters raises serious difficulties with regard to pH measurements, charge-imbalance calculations, and nonideality corrections during speciation calculations. Calculations of saturation indices for, acid mine waters commonly indicate saturation to supersaturation with respect to ferrihydrite, gibbsite, and barite and reflect a solubility control by these minerals.

INTRODUCTION

By 1985, extraction and beneficiation of copper, iron, uranium, and phosphate had generated about 1.3 x 10^9 metric tons of waste from nearly 500 mines, most of which are located west of the Mississippi River (U.S. Environmental Protection Agency, 1985). However, this is only about 2.5 percent of the total accumulated mining waste. The Clark Fork Complex near Butte, Mont., is the largest complex of Superfund sites and it reflects the greatest environmental damage of any mining site in the western United States (Moore and Luoma, 1990). More than 2 x 10^8 cubic meters of tailings have accumulated and more than 200 kilometers of the Clark Fork River have been contaminated.

Many of these wastes are producing acid waters with high concentrations of iron, copper, zinc, cadmium, arsenic, and sulfate. The most acidic mine drainage known in the U.S. is from Iron Mountain, Shasta County, Calif., where pH values below -1.0 and maximum concentrations of iron of 141 g/L (grams per liter) (fig. 1), zinc 24 g/L, copper 4.8 g/L, arsenic 340 mg/L (milligrams per liter), cadmium 211 mg/L, and sulfate 760 g/L have been determined. Mine waste contaminants may enter ground waters and surface drainages where they degrade the water quality and kill freshwater organisms.

Chemical modeling can be an effective tool in improving our understanding of the processes of acid mine water formation, the processes of metal attenuation and dispersion, and the mitigation of these processes. The results from chemical models, when combined with hydrogeological, ecological, engineering, and economic analyses, can improve assessments of risks and remedial action alternatives by water quality managers. This paper presents some of the recent advances in the application of chemical models to field sites contaminated by mine wastes and problems encountered when measuring pH, speciating acid mine waters, and calculating saturation indices.

CHEMICAL MODELING STRATEGIES

The strategy or methodology of applying chemical models to water-rock interactions is more fundamental than the particulars of the computer code or the data base. The two extremes of strategies are simulation (or forward) modeling, which is most useful when no observational data, other than initial conditions, are available and inverse modeling (Plummer, 1984), which requires site-specific field data on water chemistry, mineralogy, and isotopes. Forward modeling assumes that enough is known about water-rock interactions to make useful predictions for a given system with only initial conditions provided. Inverse modeling assumes that enough field data have been collected to determine a consistent set of geochemical processes for a given site. Of course, simulations and inverse modeling are commonly applied to any given site investigation, but the main emphasis is usually on one or the other. As science evolves, the knowledge gained from inverse modeling will improve the usefulness of forward modeling.

Both modeling strategies employ one or more of six types of computation: speciation, mass balance, thermodynamic (equilibrium) mass transfer, kinetic mass transfer, incremental reaction progress (equilibrium, kinetic or both), and adsorption. All of these can be applied to the interpretation of chemical reactions in acidic mine-water environments.

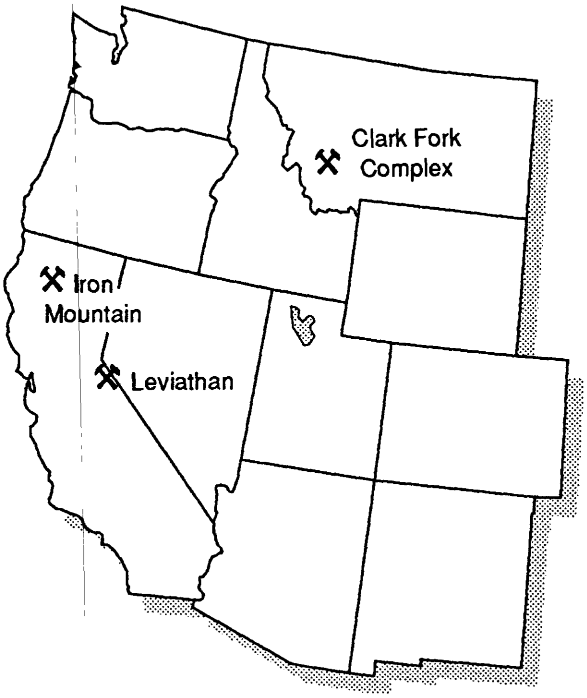

Figure 1. Location of Iron Mountain, Clark Fork Complex and Leviathan mines in the western United States.

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[1] U.S. Geological Survey, Menlo Park, Calif.

MODELING THE FORMATION OF ACID MINE WATERS

The pH of the vast majority of acid mine waters is in the range of 2 to 4, and only rarely is their pH less than 2.0. The pH is controlled by the rate of oxidation, the rate of water flow, and the availability of sulfide minerals. It may, however, be more than a coincidence that the two main constituents of acid mine waters, iron and sulfate, have hydrolysis constants operative near a pH of 2:

(a) $Fe^{3+} + H_2O = = > Fe(OH)^{2+} + H^+$ $pK_1 = 2.2$

(b) $HSO_4^- = = > SO_4^{2-} + H^+$ $pK_2 = 2.0$

Mine waters that form at pH < 2.0 actually increase in pH as the dissolved iron oxidizes because the oxidation reaction consumes acidity:

$$Fe^{2+} + 1/4O_2 + H^+ == > Fe^{3+} + 1/2H_2O$$

A challenging test of a chemical model is to attempt to reproduce an acid mine water composition given a specified mass of oxygen, water, and pyrite. This test was done for the main effluent water of the Richmond portal at Iron Mountain using forward modeling with the PHREEQE program (Parkhurst and others, 1980) after doing inverse modeling with the WATEQ4F program (Ball and others, 1987) and the BALANCE program (Parkhurst and others, 1982). The test amounted to reproducing the final effluent pH after dissolving pyrite and other minerals to the extent necessary to reproduce the effluent composition. The result is shown graphically in figure 2 and based on the work of Alpers and Nordstrom (1990) and Nordstrom and Alpers (U. S. Geological Survey, written commun., 1990). Chalcopyrite and sphalerite are oxidized along with pyrite; calcite, sericite, chlorite, and kaolinite are dissolved, increasing the pH slightly; and amorphous silica and melanterite precipitate. The simulated pH of 0.46 nearly matches the observed pH of 0.48 and gives credence to the chemical assumptions and data base used in the model. The results are most sensitive to the amount of oxidation and the composition of any iron-bearing mineral phase that precipitates from the effluent water. The acid mine effluent at Iron Mountain is so strongly acidic because maximum quantities of oxygen are reacting with a massive sulfide mineral deposit of 95 percent or more pyrite. The rate of acid production overwhelms the buffering capacity of the reactions (a) and (b) above. A further application of forward modeling by Nordstrom and Alpers (U.S. Geological Survey, written commun., 1990) was an estimate of the ground-water composition at Iron Mountain if the mine workings were plugged.

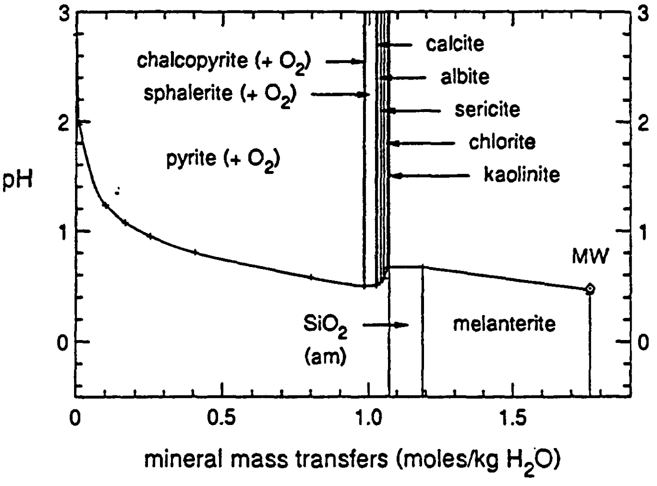

Figure 2. Forward modeling of acid mine water from Iron Mountain, Calif., plotted as changes in pH as a function of mineral mass transfer.

Forward modeling of acid mine water production is not viable without detailed knowledge of the distribution, concentration, grain size, and exposed surface area of pyrite, the transport properties of ground water, and the transport properties of oxygen. The uncertainties associated with this information, even if available, are so great as to hinder useful forward modeling. Alternatively, forward modeling can be done as a test of inverse-modeling computations, as described above. This procedure examines the reliability of our chemical models and adds to the accumulating knowledge of water-rock interactions.

INHERENT PROBLEMS IN MODELING ACID WATERS

Some of the difficulties faced when modeling the chemistry of acid mine waters are the same as those for any natural water, but those described below are inherent to the nature of acid waters. Three major problems have been encountered: (1) measurement of pH below 1.0, (2) calculation of charge imbalances, and (3) estimation of stability constants and activity coefficients.

For pH values <1.0, there is no standard definition of pH, there are no commercial standard buffers, strong acids exhibit nonideal behavior at high concentrations, and acid anions may interfere at the hydrated glass-electrode surface. These problems have been mostly resolved by the work of Nordstrom and Alpers (U. S. Geological Survey, written commun., 1990) using Pitzer's analysis of sulfuric-acid solution (Pitzer and others, 1977) to define pH and standardized sulfuric-acid solutions as buffers. This approach permitted measurement of pH to -0.50 in acid mine waters.

Ionic charge imbalances are a good check on the reliability of water analyses and should be within 10 to 20 percent. In acid waters, H^+ is a major contributor to the cation normality sum. Protons, however, cannot be directly determined. Acidity titrations are not reproducible and involve heterogeneous, kinetically controlled precipitation reactions. Most computer programs determine H^+ concentration from pH using some assumed theoretical value for the activity coefficient and accounting for pH-related complexes such as HSO_4^-. Therefore, charge-imbalance computations require a chemical model that yields accurate speciation data.

The typically high ionic strength, high sulfate concentrations, and high polyvalent cation concentrations in acid mine waters may promote strong ion-ion interactions. For some of these interactions, the stability constants may not be well-known or it may be necessary to use the Pitzer approach (Pitzer, 1977). Unfortunately, Fe(III) interaction parameters have not been determined for sulfuric acid solutions, so that the Pitzer approach will be incomplete. Reardon and Beckie (1987) and Reardon (1988) have evaluated the Pitzer parameters for Fe(II) and Al in sulfuric acid solutions, respectively. Using these data, Blowes and Jambor (1990) have modeled strongly acidic waters in mine-tailings piles.

A recent update of stability constants useful for water chemistry has been compiled (Nordstrom and others, 1990) that contains equilibria relevant to acid mine waters. The recent study of jarosite solubility by Alpers and others (1989) has provided a progress report on thermodynamic data relevant to the major solid-solution substituted jarosite solubilities. Jarosite and iron oxide hydroxides are probably the most common iron-alteration products of oxidizing sulfide assemblages.

REDOX-SPECIATION DISEQUILIBRIA

Redox couples in natural waters are notorious for being out of equilibrium (Morris and Stumm, 1967; Nordstrom and others, 1979; Lindberg and Runnells, 1984). Most computer programs, however, treat redox reactions as if they are in equilibrium. Two notable exceptions to this are EQ3/6 (Wolery and others, 1990) and WATEQ4F version 2.0 (Ball and others, 1987; Ball and Nordstrom, 1991). WATEQ4F is a speciation program that has been modified for use with acidic mine waters as well as normal ground and surface waters. It has the capability for doing independent redox speciation for Fe(II/III), O_2/H_2O, S(-II,0,VI), N(-II,III,V), As(0,III,V), Se(-II,IV,VI) and U(IV,V,VI), or to couple any combination of these for an equilibrium computation.

Speciation computations that allow redox disequilibrium have shown that the platinum-electrode Eh measurements of most acid mine waters determined by the Fe(II/III) activity ratio are as small as about 10^{-5} molars in dissolved Fe(II) and Fe(III) (Nordstrom and others, 1979; Ball and Nordstrom, 1989). Below this concentration, a deviation is caused by the effect of oxygen on the platinum electrode, and measured Eh shows no correlation with the Fe(II/III) activity ratio. Other redox couples, such as As(III/V) and Se(IV/VI), have no influence on an electrode Eh measurement (Runnells and Lindberg, 1990; Runnells and Skoda, 1990). Indeed, only iron and sulfide ions are likely to produce a quantitative Nernstian response to redox electrodes (platinum, gold, glassy carbon).

MINERAL SATURATION STATES IN ACID MINE WATERS

Acid mine waters are metal-rich sulfuric-acid solutions; hence, if they reach saturation, they are likely to precipitate insoluble metal-sulfate minerals and metal-hydrolysis products. The two most common metals in precipitates are iron and aluminum. Aluminum geochemistry is relevant in acid precipitation research because of the high solubility and mobility of aluminum in acidic solutions and its detrimental effect on fish populations. The thermodynamic data for inorganic solid and aqueous species of aluminum have recently been reviewed and evaluated (Hemingway and Sposito, 1989; Nordstrom and May, 1989).

Aluminum concentrations in freshwaters have been shown to approximate the stoichiometric solubility of microcrystalline gibbsite for pH >5.0 (Driscoll and others, 1984; Nordstrom and Ball, 1986) and aluminum commonly behaves conservatively at lower pH values. The stabilities of some of the more important basic aluminum sulfate minerals have been reviewed (Nordstrom, 1982), but clear evidence of their control on aluminum concentrations in acid mine waters is lacking.

Iron concentrations are more difficult to interpret because ferric iron hydrolyzes to form colloidal particles that are smaller than standard membrane pore sizes and because iron is present in two oxidation states, II and III. Speciation calculations with WATEQ4F on water samples from the Leviathan mine drainage system (Ball and Nordstrom, 1989) reflect a control on iron concentration by the precipitation of ferrihydrite but the log $(\alpha_{Fe^{3+}}/\alpha_{OH^-})$ slope could be interpreted as less than 3, as seen in figure 3. The slope is close to 2.35, that found by Fox (1988) in his study of suspended ferric hydroxide particles in an estuarine environment. This result suggests that sulfate ions may be an integral part of the suspended iron particles. If this is correct, then adjustments have to be made in the calculation of the ion-activity product. The apparent supersaturation with respect to ferrihydrite commonly found in acid mine waters and some ground waters may have resulted from incorrect characterization of the solid phase. Bigham and others (1990) have shown that a poorly crystalline ferric oxyhydroxide sulfate phase does precipitate from acid mine waters.

Barite is another common mineral that exhibits saturation to supersaturation in acid mine waters. Barite saturation indices commonly demonstrate a solubility control but tend to be supersaturated up to nearly one order of magnitude for the Leviathan data. A sensitivity analysis indicated that the supersaturation was real and not an artifact of the analytical or thermodynamic uncertainties (Nordstrom and Ball, 1989).

SUMMARY

Chemical modeling has been successfully applied to the interpretation of metal mobility in acidic mine waters from mine waste sites of the western United States. Results show that, under very low pH conditions (<1.0), problems are encountered with measuring pH, calculating charge-imbalances, and applying activity-coefficient corrections. Although forward (or simulation) modeling usually cannot be applied because of insufficient information, it is useful as a check on inverse-modeling techniques. This approach has been applied to the most acidic drainage in the United States at Iron Mountain, Calif.

Geochemical controls on iron, aluminum, and barium concentrations have been examined with chemical-modeling techniques in the Leviathan mine-drainage system to show the effect of solubility controls by microcrystalline gibbsite, ferrihydrite and barite.

Combining chemical models with surface water transport models will enhance the ability to predict quantitatively the fate of trace elements in surface waters affected by acid mine drainage.

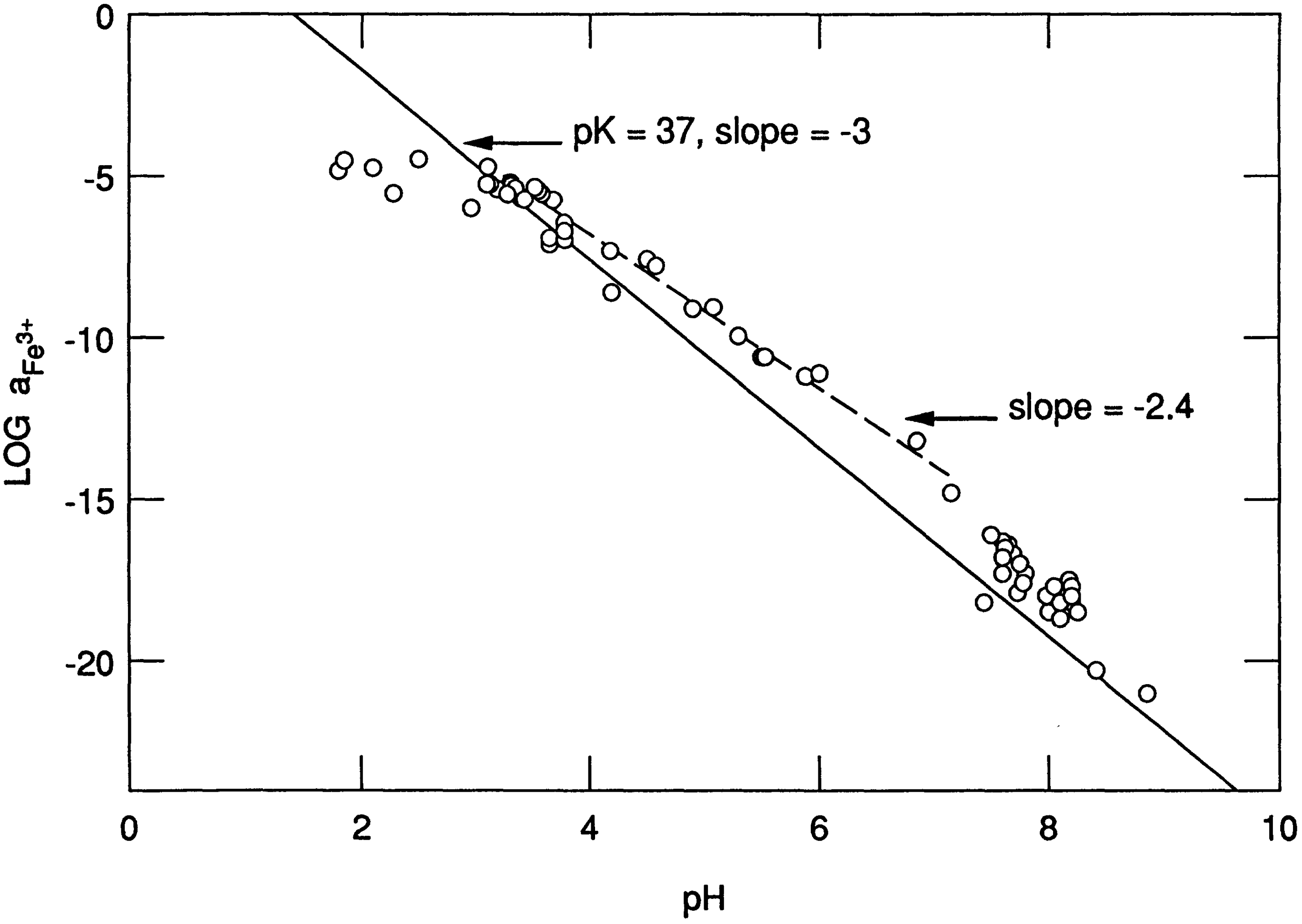

Figure 3. Plot of ferric-ion activity against pH for Leviathan mine waters with theoretical slope for ferrihydrite added (see text).

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A NEW METHOD FOR DETERMINING SOIL MACROPOROSITY

By R.W. Healy[1], G.M. Reimer[1], J.M. Been[1], *and* S.L. Szarzi[1]

ABSTRACT

Results of air-permeability and gas-tracer tests, along with measurements of air-filled porosity, can be used to develop models of continuous pore space within soils. These models can then provide a convenient framework for studying the spatial and temporal variability of macropores in the field as well as provide insight to water and solute movement through macroporous soils.

Air-permeability and gas-tracer tests were conducted in the laboratory on uniformly packed columns of silica sand and silt loam. A dilute mixture of helium and air was used as the tracer gas. Simulated macropores were constructed from stainless-steel tubes and were inserted into the columns. Results of tests were noticeably affected by the presence or absence of macropores. Permeability of the soils was slightly increased by the presence of the macropores. In terms of tracer-test results, breakthrough curves for soils that contained macropores had two concentration peaks. The first peak occurred quickly following tracer injection. The second peak was similar in magnitude and timing to the single peak obtained in tests from the same soil in the absence of any macropores.

INTRODUCTION

The importance of preferential flow paths in the travel of water and solutes through soils has been widely recognized for more than 100 years (Lawes and others, 1882). Water may move more rapidly through these flow paths than through the bulk soil matrix. The chemistry of ground waters underlying agricultural fields can be greatly affected by the presence of preferential flow paths. The rapid movement of water from land surface to aquifers affords little opportunity for degradation, adsorption, or plant uptake of surface-applied agricultural chemicals.

Preferential flow paths may develop in response to a number of factors, including variability in hydraulic properties of soils, such as layering of different soils or innate heterogeneity of a single soil; instability of wetting-front movement, which produces fingering through coarse-grained sediments; and the presence of macropores. Macropores are defined as large, continuous holes that may channel the flow of water. They can be formed by plant activity (root channels), animal activity (earthworm holes), or other natural processes such as drying (dessication cracks) and geological activity (rock fractures).

Although a great deal of research has been devoted toward characterizing macropores and quantifying their influence on the movement of water and solutes through soils, there are still large gaps in our understanding of these topics. Detailed characterization of individual macropores has been conducted only in the laboratory on small cores using time-consuming and expensive techniques such as computed tomography (Warner and others, 1989). Adaption of these techniques for use in the field is not considered feasible. Water movement through a single macropore of uniform geometry can be described by existing theory, however, there is no such theory to describe water movement through a complex network of interconnected macropores. Little information has been reported on the spatial and temporal variability of macropores within any field.

This paper presents details of a method for identifying the presence of macropores in soils. The method has been developed for use in the field, but only results obtained from laboratory experiments will be presented here. The method is based on determining air-filled porosity, intrinsic permeability, and traveltime of a tracer gas through soil. This information can then be used to develop and test models of macropore geometry and distribution. These models should be useful for describing spatial and temporal variabilities of macropores in the field, as well as for developing an understanding of water and solute movement through field soils.

The use of air and gas tracers to study macroporosity has several advantages over the use of water and solute tracers. Gases will not affect ambient soil-moisture contents or soil structure. Water may cause expansion of clay particles and therefore alter the macropore network. Experiments with gases can be conducted quickly. Insoluble gas tracers can be removed from the tested soil much more easily than liquid tracers, thus experiments can be easily replicated on the same soils.

Air permeability was used by Buehrer (1932) and Reeve (1953) as an indicator of soil structure. Currie and Rose (1985) demonstrated that gas-diffusion coefficients are related to soil structure. Using soil cores, Ball (1981) measured soil-gas diffusivity, air permeability, and air-filled porosity at different soil-water tensions and used the information to evaluate two models for describing continuous air-filled pores. Blackwell and others (1990) used permeability and air-filled porosity to characterize the structure of macroporous clay soils.

METHODS

Laboratory experiments were conducted in 113-L (liter) steel drums (0.46 m (meter) diameter, 0.70-m length). The drums are sealed on the top and bottom except for small ports for injection and sampling of gases and for pressure measurements. The bottom 6 centimeters of each drum was packed with coarse pea gravel to allow efficient mixing of injected gases. A permeable geofabric was placed on top of the gravel and the drum was filled with a selected test soil. The soil was air dried and packed to a uniform bulk density. Simulated macropores constructed of stainless-steel tubes were placed vertically in the drums. They were variable in number and length and extended from the top of the drum to different depths, depending on the particular experiment.

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Table 1. *Results of air-permeability and tracer tests*

[T(.01) is time after tracer injection at which sampled gas reached a relative concentration of 0.01]

Soil type	Simulated number	macropores diameter, in centimeters	Permeability, in square centimeters	T(0.01), in seconds	Air-filled porosity
Sand	0	--	1.5 E-07	600	0.42
Sand	7	0.318	1.6 E-07	530	.42
Sand	5	.635	6.0 E-07	60	.42
Sand	10	.635	6.0 E-07	60	.42
Loam	0	--	6.9 E-08	630	.48
Loam	3	.318	1.4 E-07	70	.48
Loam	7	.318	3.7 E-07	30	.48
Loam	10	.635	4.0 E-07	20	.48

Permeability was determined from Darcy's equation after injecting air through the drum at a fixed mass-flow rate and monitoring temperature and the pressure difference between the top and bottom of the drum. Gas-tracer tests were conducted using helium (He) and air to give a mixture of 80 ppm (parts per million) He in air. The tracer gas was released from a pressurized vessel through the bottom port of the drum. Gas samples were obtained through the top port and analyzed on a mass spectrometer for He concentration (Reimer and others, 1979). Air-filled porosity was obtained from moisture-retention curves and measured soil-water tensions.

PRELIMINARY RESULTS

Two soils were tested in the laboratory drums: a silica sand (porosity of 0.42, bulk density of 1.53 g/cm^3 (grams per cubic centimeter) and a silt loam (porosity of 0.50 and bulk density of 1.33 g/cm^3). Table 1 shows permeability and the time between tracer injection and attainment of a relative tracer concentration of 0.01 at the top of the drum. For these tracer tests, 8 L of tracer gas were instantaneously released to the bottom of the drum from a vessel that was pressurized to 1 kilopascal above atmospheric pressure. The simulated macropores extended through the entire thickness of the soil. Two typical breakthrough curves, showing the relative concentration of He at the top of the drum as a function of time, are displayed in figure 1. The presence of the simulated macropores produced a slight increase in the permeability of the soils, but had a large effect on the tracer breakthrough curves. In the absence of macropores, tracer breakthrough curves displayed a smooth slope and a single peak concentration. It took several minutes for He concentration at the top of the drum to rise above background values. When macropores were present, the breakthrough curves contained two concentration peaks. The first peak usually occurred less than one minute after injection; the second peak was similar in magnitude and timing to the peak obtained for the same soil without macropores.

SUMMARY AND CONCLUSIONS

Air-permeability and air-filled porosity measurements, along with gas-tracer tests, are proposed as a means for developing models of continuous pore space within soils. Such models can serve as a framework in which simple field measurements can be used to describe the characteristics and distribution of macropores. Hence, it may be possible to study the spatial and temporal variabilities of these characteristics in selected fields. Once models that represent macropore networks are developed, models of water flow and solute transport through such networks can be constructed.

Air-permeability and gas-tracer tests were conducted in the laboratory on uniformly packed drums containing either silica sand or silt loam. The tracer gas consisted of 80 ppm of He in air. Gas samples were analyzed on a mass spectrometer. Simulated macropores, in the form of stainless-steel tubes, were inserted into the drums. Preliminary results indicate that permeability of

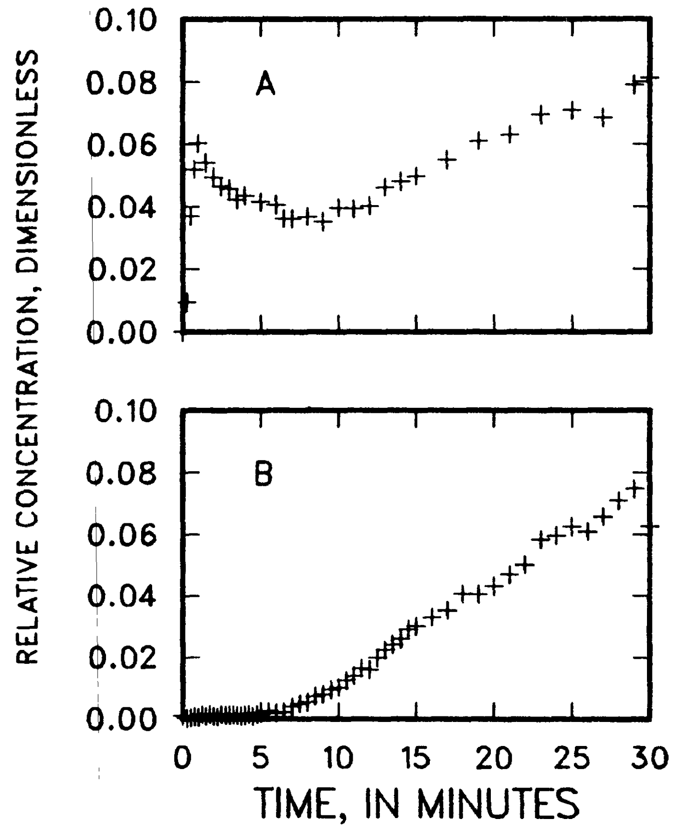

Figure 1. Breakthrough curves for two gas-tracer tests: (A) silt loam with 7 simulated macropores of 0.318-centimeter diameter, and (B) silt loam with no macropores.

the soils increased slightly due to the presence of macropores. Tracer breakthrough curves were greatly affected by the presence of macropores. When macropores were present, breakthrough curves showed a sharp initial rise followed by a second peak whose magnitude and timing was similar to the single peak obtained in tests on the same soil without macropores.

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CHLOROFLUOROCARBONS (CCl_3F AND CCl_2F_2): USE AS AN AGE-DATING TOOL AND HYDROLOGIC TRACER IN SHALLOW GROUND-WATER SYSTEMS

By Eurybiades Busenberg[1] *and* L. Niel Plummer[1]

ABSTRACT

Procedures have been developed for sampling ground water for trace levels of chlorofluorocarbons (CFC's, Freons[2]). Samples are collected and stored in 50 milliliter borosilicate glass ampules that are sealed at the well site in an environment isolated from air and free from CFC's. CFC concentrations, which remain stable in the sealed glass ampules for many months, are determined using purge-and-trap gas chromatography with an electron-capture detector to less than 1 picogram per kilogram. The analytical procedures are relatively simple, inexpensive, and require about 10 minutes per sample.

The procedure was applied to water samples from shallow Quaternary alluvium and terrace deposits in central Oklahoma. Results of CFC age-dating of about 400 samples show that CFC's are generally consistent with tritium data and can be extremely useful tracers and age-dating tools in hydrologic studies. Preliminary CFC-model age dating indicates that, in the past 40 years, there may have been two major periods of significant ground-water recharge in central Oklahoma. The first significant period of recharge occurred in the years 1945-60, and the second in 1967-75. The results indicate that much less recharge may have occurred in the drought years 1960-67. Precipitation and tritium data are consistent with this conclusion derived from the CFC's, CCl_3F (F-11), and CCl_2F_2 (F-12) model age-dating. The precipitation record indicates that another wet period may have occurred in the mid-1980's that was not recognized. This water may reside in the unsaturated zone or may have not yet intercepted the well-screens of domestic and municipal wells completed in the alluvium and terrace deposits.

Several areas of ground water with F-11 and(or) F-12 concentrations in excess of that in equilibrium with modern air have been identified in the alluvial and terrace deposits of central Oklahoma. One area originates within the Oklahoma City limits and extends for several kilometers along the North Canadian River. Another major area originates southeast of the city of Norman and extends more than 20 kilometers along the Canadian River. There may be some correlation between these observed CFC anomalies, high population densities, the geographical location of sewage-disposal ponds, and sewage returns into rivers and streams. It is conceivable that some of the CFC contamination may result from the seepage of sewage effluent (with high concentrations of CFC's) into the alluvial and terrace deposits.

The preliminary results from the shallow unconfined ground waters in Pleistocene sands of the Delmarva Peninsula indicate that there is very little contamination of the shallow aquifers with CFC's. Contamination levels in central Oklahoma are significantly greater than those observed on the Delmarva Peninsula. Model CFC ages for waters from Fairmount, Del., also appear to be consistent with tritium concentrations in the ground waters.

INTRODUCTION

Chlorofluorocarbons (CFC's) are extremely stable synthetic organic compounds. They were first manufactured in the 1930's, and are believed to be entirely of anthropogenic origin (Lovelock, 1971). Presently, more than 10^9 kilograms of CFC's are produced annually and are used as refrigerants, aerosol propellants, cleaning agents, solvents, and blowing agents in the production of foam rubber and plastics. CFC's are eventually released into the atmosphere and hydrosphere. Residence times in the atmosphere are approximately 60 and 120 years for F-11 (CCl_3F) and F-12 (CCl_2F_2), respectively (Derra, 1990).

The use of CFC concentrations in natural waters as potential dating tools was recognized in the mid-1970's. Thompson (1976) and Thompson and Hayes (1979) measured the F-11 content of ground waters from southern New Jersey, Arkansas, and south-central Texas, and reported good qualitative agreement with the known hydrology and tritium concentrations in these three localities. In these studies, CFC's were also found useful in detecting mixing of very small quantities of modern water with old waters, and detecting contamination of ground water. The presence of CFC's in ground water indicates recharge after the 1950's, or mixing of older waters with post-1950's water. Little else has been done recently to evaluate the full potential of CFC's in ground water (Randall and Schultz, 1976; Thompson and Hayes, 1979). The picture is completely different in oceanographic studies where CFC's are routinely used for dating and tracing water masses. An important reason for this success has been the ability to sample and immediately measure the CFC concentrations at sea without contaminating the samples (Bullister and Weiss, 1983). In early ground-water studies, F-11 was measured on site (Thompson and Hayes, 1979). Today it is difficult to perform the analyses in the field due to Nuclear Regulatory Commission licensing requirements for the radioactive nickel-63 in the electron-capture detector (ECD). In this study, the problems of contamination and preservation of uncontaminated natural waters were solved by isolating the samples from air (modern air uncontaminated by local sources of CFC's contains at least 475 pptv [parts per trillion, volume per volume] F-12 and 275 pptv F-11, respectively) and storing the sample in borosilicate glass (Reynolds and others, 1990) ampules that are welded closed at the well site for subsequent laboratory analysis.

This paper describes a method for collecting and analyzing ground-water samples for trace-level concentrations of F-11 and F-12. The procedures necessary to evaluate the CFC results are discussed. Examples from central Oklahoma and Fairmont, Del., are given to illustrate the age-dating potential of this method.

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[1] U.S. Geological Survey, Reston, Va.

[2] The use of brand, firm, or trade names in this paper is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

ACKNOWLEDGMENTS

The assistance of S. C. Christenson, D.M. Ferree and staff of the USGS Central Oklahoma National Water-Quality Assessment Program study; L.J. Bachman, USGS Towson, Md.; and J.M. Denver, USGS, Dover, Del., is gratefully acknowledged.

EXPERIMENTAL METHODS

An apparatus was developed for collecting and sealing water samples in borosilicate glass ampules without allowing the sample to come in contact with air, plastics or rubber. Ultrapure nitrogen (N_2) gas flow keeps air out of the apparatus and ampule. The neck of the ampule is immediately welded shut with an oxygen-MAPP gas torch about 2 cm above the ampule water level while connected to the sampling apparatus. Three to six samples were collected at each well at time intervals of 5 to 20 minutes.

The CFC analytical system is a modified version of the original design of Bullister and Weiss (1988), where a detailed description of the analytical system can be found. In our analytical system, an argon methane mixture was used as the carrier gas, and ultrapure N_2 was used as the stripping gas. Procedures and an apparatus were developed to inject the water samples into the stripping cell, without allowing any contact with the laboratory atmosphere. The concentrations of F-11 and F-12 are measured with an ECD. From the CFC concentrations in the water sample, the temperature, the volume of water, and headspace of the ampule, the concentration of halomethanes in the aquifer are calculated. From the concentrations of F-11 and F-12 in the samples and the recharge temperature, the atmospheric-equilibrium partial pressures can be calculated (Warner and Weiss, 1985).

DATING NATURAL WATERS WITH CCl_3F AND CCl_2F_2

The CFC model age of the ground water is obtained from F-12 and F-11 levels in the samples and is taken as the time in which the recharge water became isolated from the atmospheric source of CFC's. Using the observed CFC concentration and the recharge temperature, the atmospheric partial pressures of the two CFC's are calculated by means of Henry's Law. These partial pressures are compared to the modeled atmospheric growth of CFC's (fig. 1) to obtain the apparent age of the ground water. The post-1975 atmospheric levels for F-11 and F-12 were reconstructed mainly from the continuous data collected by National Oceanic and Atmospheric Administration (Elkins, 1989). Pre-1975 levels have been estimated from the CFC-production records of the Chemical Manufacturers Association. Figure 1 also includes the March tritium concentrations in precipitation for central Oklahoma (Michel, 1989) adjusted for radioactive decay to 1988. This model assumes that F-11 and F-12 concentrations in the recharge water were proportional to the tropospheric concentrations at any particular time and location. The model implies that uncontaminated recharge water possesses unique F-11 and F-12 concentrations that depend only on tropospheric CFC concentrations and temperature, and are not contaminated by local near-surface anomalies. The historical reconstruction of the average monthly air temperatures and precipitation records were obtained from Karl and others (1990).

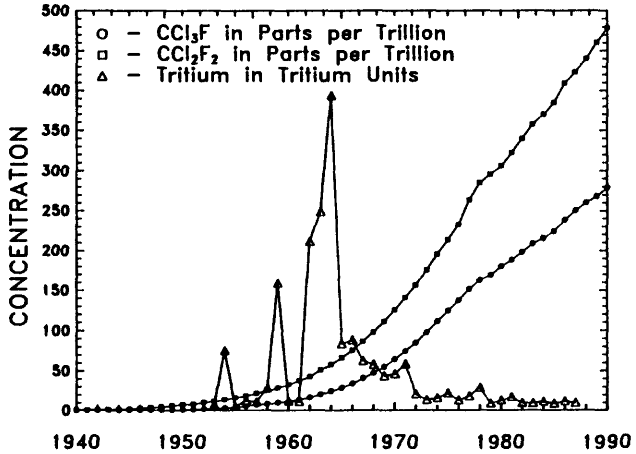

Figure 1. Atmospheric concentrations of CCl_3F and CCl_2F_2 for central Oklahoma as a function of time. The March tritium concentrations in precipitation are also shown. Tritium was adjusted for radioactive decay to December 31, 1988.

Valid CFC model dates can be obtained only if the following conditions are satisfied (1) the aquifer was not contaminated by local sources of CFC's, (2) the water sample analyzed was not contaminated during collection, (3) the water sample contains CFC concentrations that are representative of the concentrations present in the aquifer, (4) the CFC concentrations in the aquifer were not modified by geochemical or biological processes, and (5) the aquifer does not contain large amounts of organic material. The CFC concentrations were not corrected for advective dispersion resulting from the transport by the ground water--that is, the water was assumed to move by plug flow. The CFC model ages should be regarded as minimum estimates because of the possibilities of contamination of the ground water or chance introduction in the sampling process--this is particularly important for old waters that contain very low concentrations of CFC's. Under optimal conditions, the assigned age has an uncertainty of approximately 3 years.

RESULTS AND DISCUSSION

Chlorofluorocarbons and Tritium Concentrations as Indicators of Ground-Water Age

The chemistry of ground water of the central Oklahoma Quaternary alluvium and terrace deposits has been described by Parkhurst and others (1989). Figure 2 shows the frequency distribution of F-11 and F-12 concentrations in the Oklahoma ground-water samples. The F-12 concentrations are higher than F-11 concentrations in the wells sampled. This distribution pattern is the exact opposite of what is expected considering the atmospheric partial

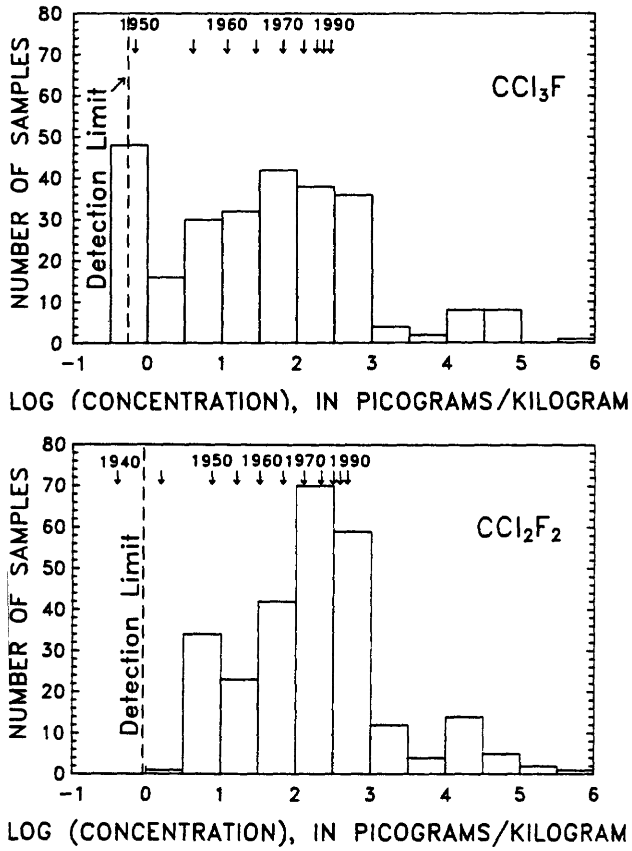

Figure 2. The frequency distribution of samples as a function of their log CCl_3F (2A) and log CCl_2F_2 (2B) concentrations. The model chlorofluorocarbon ages for uncontaminated samples are also given. A 9 degree Celsius recharge temperature was used in the calculations.

pressures and Henry's Law coefficients of these two CFC's. The model CFC's ages for uncontaminated samples at an assumed 9 degrees Celsius recharge temperature are also given in figure 2. Representative data from central Oklahoma and Fairmount, Del., are presented in table 1. Note that very old uncontaminated waters have no tritium and generally undetectable or very small CFC concentrations. Waters with CFC model ages in the 1960's have the highest tritium levels observed in both Oklahoma and Delaware. The waters with CFC model ages in the 1970's and 1980's, have intermediate tritium levels and the highest CFC concentrations. The rationale used in assigning the various ages is briefly described below. For waters from both the Bethany and Cook wells, the F-11 and F-12 model ages are consistent with the tritium results; these ground waters clearly are older than the late 1940's, at the detection limits of the CFC method. The presence of small amounts of F-12 is probably related to well construction, allowing mixing of small amounts of shallow ground water with older formation water during pumping. Water from the Allred well represents a sample that is highly contaminated with F-12; it is likely that this sample is contaminated to a lesser extent with F-11. Therefore, the early 1950's F-11 model age should be considered a minimum age, and very possibly it is significantly older. The F-11 and F-12 model ages give an early 1950's date for ground water at the Harrah well. The Harrah and Allred dates are clearly unreliable. Dates may not be consistent with the tritium data for one or more of the following reasons: (1) The well was not properly purged, (2) the samples were contaminated with modern air, and(or) (3) the water sampled is a mixture of older CFC-free water with younger water. If Harrah water is a mixture, mass-balance considerations on both CFC's and tritium require

Table 1. *Typical results of CCl_3F, CCl_2F_2 and tritium obtained in this study from central Oklahoma and the Delmarva Peninsula*

[<, less than; >, greater than; picog/kg, picogram per kilogram; TU, tritium units; °C, degrees Celsius]

Well name	Depth or screen (feet)	Tritium (TU)	F-11 picog/kg	F-12 picog/kg	Recharge Temp. in °C[1]	Model[2] F-11 age	Model F-12 age
			Central Oklahoma				
Bethany G-1[3]	822' TD	<.1	0.0	3.3	9	<L1940's	L1940's
Cook	70' TD	<.1	.0	3.0	9	<L1940's	L1940's
Allred	111' TD	<.1	6	70,000	9	E1950's	(4)
Harrah #5[5]	325' TD	<.1	9	50	9	M1950's	M1950's
Manwell	60' TD	1.2	3	12	9	E1950's	M1950's
Fitz	80' TD	2.4	28	34	9	L1950's	L1950's
Bronson	57' TD	22.8	53	78	9	M1960's	M1960's
Berstresser	24' TD	14.7	302	133	9	E1970's	E1970's
Sweeney	45' TD	11.9	307	172	9	E1970's	M1970's
			Delmarva Peninsula				
Manokin	280-290'	<.1	72	6	5	E1960's	L1940's
Ph 13-29	75-78'	24.5	136	41	5	M1960's	E1960's
Ph 22-12	12-15'	15.2	639	204	5	L1970's	L1970's
Ph 22-11	51-54'	22.6	504	77	5	M1970's	M1960's
Pg 15-02	12-15'	13.5	610	217	5	L1970's	L1970's
Pg 15-03	66.5-69.5'	23.3	978	140	5	(3)	E1970's

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[1] The recharge temperature used influences the model CFC-age obtained. A higher temperature will yield younger model F-11 and F-12 ages.

[2] The prefix letter designations in E1960's, M1960's and L1960's indicate early, middle and late 1960's, respectively.

[3] Carbon-14 3.5 percent modern (D.L. Parkhurst, U.S. Geological Survey, written commun., 1990).

[4] The age cannot be evaluated. The sample is highly contaminated with F-11 or F-12.

[5] Carbon-14 21.0 percent modern (D.L. Parkhurst, U.S. Geological Survey, written commun., 1990).

that the amount of young water be less than 1 percent. Commonly, small discrepancies are observed between the F-11 and F-12 model ages, as demonstrated by ages of the water samples from the Manwell, Sweeney and Ph 13-29 wells. The older of the two model ages is probably the more reliable. When discrepancies between the F-12 and F-11 model ages are very large, contamination with CFC is indicated. A model age older than the oldest date obtained is implied, because, if the sample is clearly contaminated with one of the CFC's, the water is also very likely to be contaminated to a lesser extent with the second CFC. Because contamination decreases the calculated age of the water, the true ages of these samples are likely to be greater than the oldest model age. The effects of contamination are more pronounced as the CFC concentrations in ground waters decrease. The results presented in table 1 show the importance of evaluating all available hydrologic and isotopic data before assigning a CFC model date. Discrepancies between CFC age, tritium data, and other hydrologic variables can yield important information concerning the hydrology, the well construction, and(or) sampling procedures.

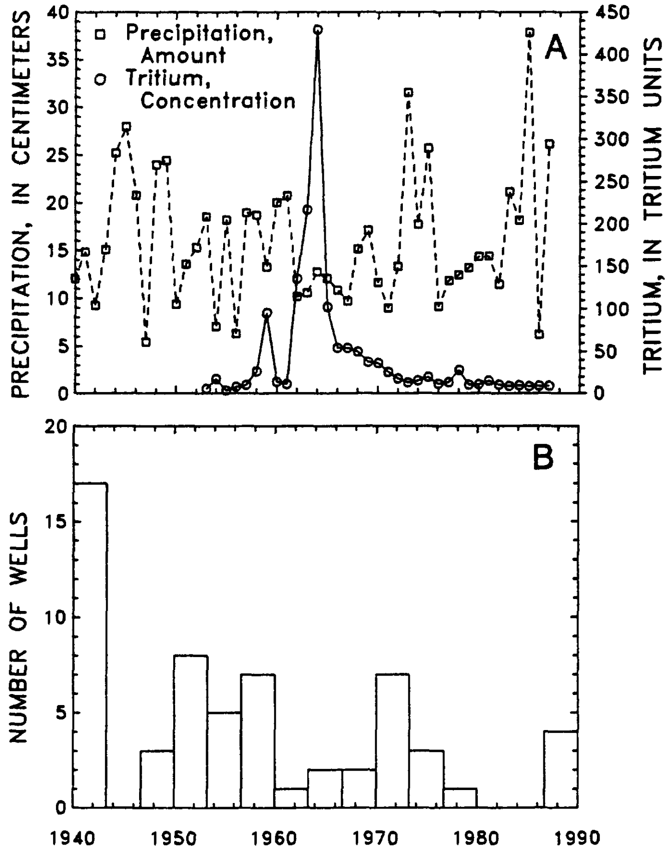

Figure 3. (A) The mean average tritium concentration in December through March precipitation in central Oklahoma as a function of time. The tritium was decayed to the year 1988. The cumulative precipitation for the recharge months of December through March for central Oklahoma as a function of time; (B) shows the frequency distribution of ground waters as a function of their chlorofluorocarbon model-ages. Note that samples with ages below the detection limits of the tritium and chlorofluorocarbon dating were assigned early 1940's ages. Ground waters less than 20 years old that are highly contaminated with chlorofluorocarbons were assigned a late 1980's date.

Estimation of Recharge from Chlorofluorocarbons and Tritium Results

Figure 3A shows the weighted annual means of tritium in precipitation for the recharge months of December through March, adjusted for radioactive decay to the year 1988, and the amount of precipitation for these same months as a function of time. The bulk of the recharge occurs in the winter months in the western United States when plants are dormant and evapotranspiration is at a minimum. A *rough* estimate of the rates of recharge can be obtained by the weighted means for precipitation for the winter months. This is by no means the best way of evaluating recharge; Pettyjohn and Miller (1982) estimated recharge of central Oklahoma from stream-hydrograph data and have shown that recharge varies considerably over such a large area in any given year. It is very likely that some recharge occurs somewhere even during periods of drought, but may be obscured by the large volumes of recharge during years of high winter precipitation.

The frequency distribution of wells as a function of CFC model age are shown in figure 3B. The CFC model ages of the ground waters were calculated from the CFC concentrations assuming that the waters were in equilibrium with uncontaminated air at the time of recharge. Where more than one date was obtained from CFC concentrations, for the same well, the oldest date was considered to be the more reliable and was used. All ground waters with tritium concentrations of <0.3 tritium units are very old but were assigned the arbitrary age of 1940-43.3 in this figure, regardless of their CFC model age. The age of these waters may be substantially greater, but an accurate age determination is beyond the capabilities of both the tritium and CFC dating methods. Most of the ground waters shown to have late-1980's ages have calculated F-11 and F-12 concentrations that are much higher than those in the present atmosphere. Based on the tritium data, these ground waters are less than 20 years old and are highly contaminated with CFC's.

Very high tritium concentrations of the early to middle 1960's, caused by atmospheric nuclear testing, were not observed in any of the wells sampled in this study. Note that this period of high atmospheric tritium corresponds to an extended period of drought, and presumably minimal recharge. A less severe period of drought occurred during 1976-83. The results shown in figure 3B may be biased inasmuch as each well represents one point and the combined results of the sampling may not be representative of the true ground-water-age distributions. Geographical variations in ground-water-age distributions within the study area are equally conceivable.

The frequency distribution of ground-water ages (fig. 3B) appears to be similar to the precipitation record, possibly indicating that there were two principal periods of recharge in the past 40 years in central Oklahoma, the first from the late 1940's to 1960 and the second in the early and middle 1970's. The possible recharge period of the middle 1980's (fig. 3) may still be in the unsaturated zone or is too shallow to intercept well screens in the alluvium and terrace deposits. The four wells with very large concentrations represent severely contaminated waters and do not represent this last cycle of recharge (fig. 3). Similarly, the preliminary results from the Delmarva Peninsula show a consistency between the CFC model ages and tritium concentrations.

The ground-water ages of wells can be successfully estimated by the CFC method. Even though tritium data from the wells cannot be used for precise age determinations, they are invaluable, when combined with CFC concentrations, for identifying contaminated ground waters and for confirming the age estimates. Inconsistencies between the CFC model dates and tritium concentrations, and all other available information should be resolved before an age estimate is assigned to a ground-water sample.

Areal Distribution of Anomalous Chlorofluorocarbon Concentrations in the Alluvium and Terrace Deposits of Central Oklahoma

A map of central Oklahoma study area is shown in figure 4. The stippled areas represent ground waters with high F-11 and F-12 concentrations that are supersaturated with respect to the 1990 tropospheric CFC concentrations (fig. 1). The concentrations of these anomalies are highest near the rivers and decrease with increasing distance from the streams. The largest of the contaminated areas originates within the city limits of Oklahoma City and extends along the North Canadian River. A smaller area was identified farther down stream on the North Canadian River. Two contaminated areas were identified on the Canadian River; the smaller is located south of the Oklahoma City anomaly, and the larger is southeast of Norman and extends for more than 20 km along the river. The alluvial aquifer along the Deep Fork also is somewhat contaminated with F-11 but not with F-12. These anomalously high CFC levels are located near sewage disposal ponds, treated sewage returns into streams, and urban areas. Sewage effluents are characterized by variable and high CFC's concentrations (Schultz and others, 1976) and may be the source of the observed anomalies through seepage from these disposal ponds. During flooding events, contaminated water may move from the river into bank storage and can conceivably reach some wells. Septic tanks, garbage disposal sites, improperly disposed cars, and refrigerators can also be important point sources of CFC's.

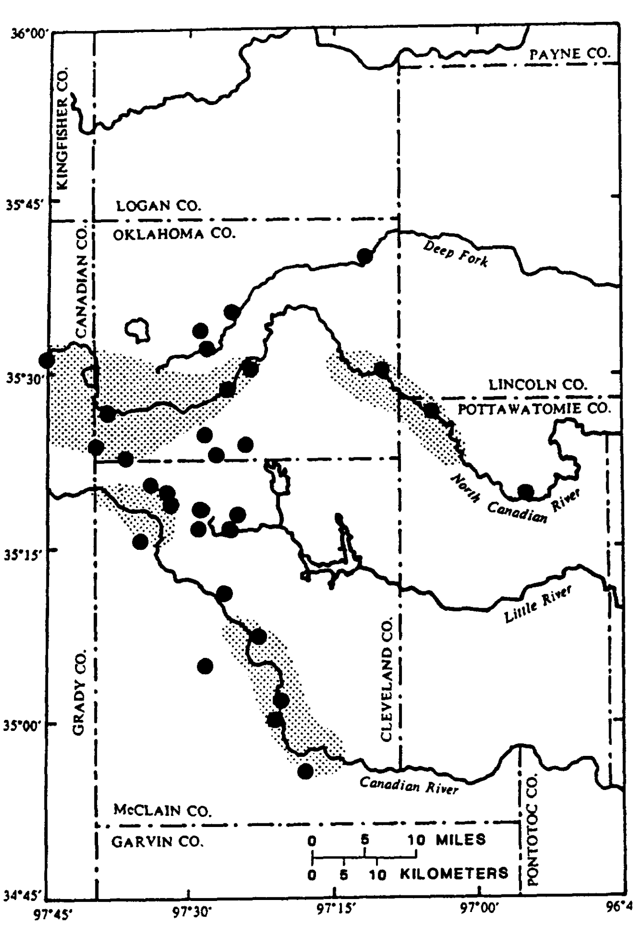

Figure 4. Map of central Oklahoma showing the areal extent (stippled area) of waters with anomalous CCl_3F and CCl_2F_2 concentrations. Filled circles are the location of sewage-disposal ponds.

Results from approximately 80 wells from the Delmarva Peninsula show that (1) very few wells are contaminated with CFC's, (2) the contamination levels are orders of magnitude smaller than those observed in central Oklahoma, and (3) the anomalies are of small areal extent. The most severe contamination found in Delmarva was near Cape Charles, Va., in few very shallow wells.

CONCLUSIONS

A method has been developed for sampling and analyzing ground waters for trace concentrations of CFC's. The procedures for sampling and analysis are relatively simple, fast, and inexpensive.

Results from central Oklahoma and the Delmarva Peninsula show that CFC's can be used to date ground waters younger than 40 years. Tritium data and other hydrological information available should be obtained. The combined results can be used to determine whether the observed CFC concentrations have been modified by contamination and thus confirm the assigned CFC dates.

CFC concentrations can be used to detect mixing of old waters with young waters and used to detect leakage between shallow aquifers, improperly set cement seals in wells, and as a tracer of post-1950 water.

Contamination of shallow ground water with CFC's was commonly found in and near urban areas of central Oklahoma. Contamination with chlorofluoromethanes is not a serious human hazard because of their low toxicities. However, many of the highly contaminated wells also contained significant concentrations of other, as yet unidentified, halogenated hydrocarbons.

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MICROBIAL REDUCTION OF URANIUM

By Derek R. Lovley[1], Elizabeth J. P. Phillips[1], Yuri A. Gorby[1], *and* Edward R. Landa[1]

ABSTRACT

The Fe(III)-reducing microorganisms, GS-15, and Shewanella putrefaciens, were found to obtain energy for growth by coupling the oxidation of various electron donors to the reduction of oxidized uranium, U(VI), to its reduced form, U(IV). Both organisms grew in high concentrations (10 millimolar) of dissolved U(VI), but also reduced U(VI) to very low concentrations (<0.4 micromolar). Studies on the stoichiometry of acetate uptake, metabolism of [2-^{14}C]-acetate, and U(VI) reduction indicated that GS-15 oxidized acetate to carbon dioxide with U(VI) as the sole electron acceptor. Hydrogen, formate, lactate, and pyruvate could serve as electron donors for U(VI) reduction by S. putrefaciens. Desulfovibrio desulfuricans also rapidly reduced U(VI) to U(IV) but could not obtain energy to support growth from this reaction. Microbial U(VI) reduction in defined media and aquatic sediments was much faster than commonly cited abiological mechanisms for U(VI) reduction. These results are of significance because the reduction of soluble U(VI) to insoluble U(IV) is an important mechanism for the immobilization of uranium in aquatic sediments and the formation of some uranium ores. Furthermore, stimulation of microbial U(VI) reduction could be a useful mechanism for the bioremediation of uranium-contaminated waters.

INTRODUCTION

Reduction of the soluble, oxidized form of uranium, U(VI), to insoluble U(IV) is an important mechanism for the immobilization of uranium in aquatic sediments and for the formation of some uranium ores (Jensen, 1958; Hostetler and Garrels, 1962; Bonatti and others, 1971; Turekian and Bertine, 1971; Langmuir, 1978; Kadko, 1980; Colley and Thomson, 1985; Cochran and others, 1986; Wallace and others, 1988; Anderson and others, 1989). U(VI) reduction has generally been regarded as an abiological reaction in which sulfide, H_2, or organic compounds function as the reductant (Jensen, 1958; Hostetler and Garrels, 1962; Langmuir, 1978; Maynard, 1983). Microbial involvement in U(VI) reduction has been considered to be limited to indirect effects such as microbial metabolism providing the reduced compounds for abiological U(VI) reduction and microbial cell walls providing a surface to stimulate abiological U(VI) reduction (Jensen, 1958; Taylor, 1979; Mohagheghi and others, 1985).

However, it is becoming increasingly clear that the reduction of metals in anaerobic environments is frequently the result of the direct enzymatic reduction of metals by bacteria (Lovley, 1987; Ghiorse, 1988; Ehrlich, 1990). For example, the Fe(III)-reducing microorganism, strain GS-15, grows under anaerobic conditions by enzymatically coupling the oxidation of acetate to carbon dioxide with the reduction of Fe(III) to Fe(II) (Lovley and others, 1987; Lovley and Phillips, 1988) according to

$$CH_3COO^- + 8\ Fe(III) + 4H_2O \rightarrow 8\ Fe(II) + 2HCO_3^- + 9H^+ .$$

Thermodynamic calculations have indicated that, per electron transferred, acetate oxidation coupled to U(VI) reduction has the potential yield more than twice the energy that is available from Fe(III) reduction (Cochran and others, 1986). This suggests that microorganisms might also be able to derive cellular energy by coupling the oxidation of organic compounds to the reduction of U(VI).

The purpose of these studies was to examine the ability of microorganisms to use U(VI) as a terminal electron acceptor. The results summarized here, which are derived from a recent publication (Lovley and others, 1991), demonstrate that some dissimilatory Fe(III)-reducing microorganisms can obtain energy for growth by means of electron transport to U(VI).

MATERIALS AND METHODS

Materials and methods are described by Lovley and others (1991).

RESULTS AND DISCUSSION

When GS-15, grown on acetate and Fe(III), was inoculated into an anaerobic medium with acetate as the sole electron donor and U(VI) as the potential electron acceptor, U(VI) was reduced to U(IV) over time (fig. 1A). Growth coincided with U(VI) reduction and stopped as U(VI) became depleted. When [2-^{14}C]-acetate was incorporated into the medium, $^{14}CO_2$ was generated in direct proportion to U(VI) reduction (fig. 1B). In a separate experiment in which acetate concentrations were measured in cultures growing with U(VI) reduction, U(VI) and acetate loss over time were linearly related (r=0.9) with a U(VI):acetate ratio of 3.6:1. Given that a small proportion of the acetate metabolized would be incorporated into cells, these results indicate that GS-15 can obtain energy for growth by oxidizing acetate with the reduction of U(VI) to U(IV) according to

$$CH_3COO^- + 4\ U(VI)\ + 4H_2O\ \rightarrow 4\ U(IV) + 2HCO_3^- + 9H^+$$

Energy conservation from acetate oxidation coupled to U(VI) reduction should be through electron-transport and oxidative phosphorylation, because there is no known mechanism to generate ATP through substrate level phosphorylation with acetate as the substrate. Subsequent studies have indicated that, in GS-15, electron transport to U(VI) proceeds through a respiratory chain containing a b-type cytochrome (Y. Gorby, U.S. Geological Survey, written commun., 1991). Thus, electron transport to U(VI) may be similar in some respects to electron transport to Fe(III) which also proceeds through a b-type cytochrome (Gorby and Lovley, 1991). GS-15 is considered to reduce U(VI) directly rather than indirectly through reduction of Fe(III) with subsequent reduction of U(VI) by Fe(II), because Fe(II) did not reduce U(VI) in the growth medium

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[1] U.S. Geological Survey, Reston, Va.

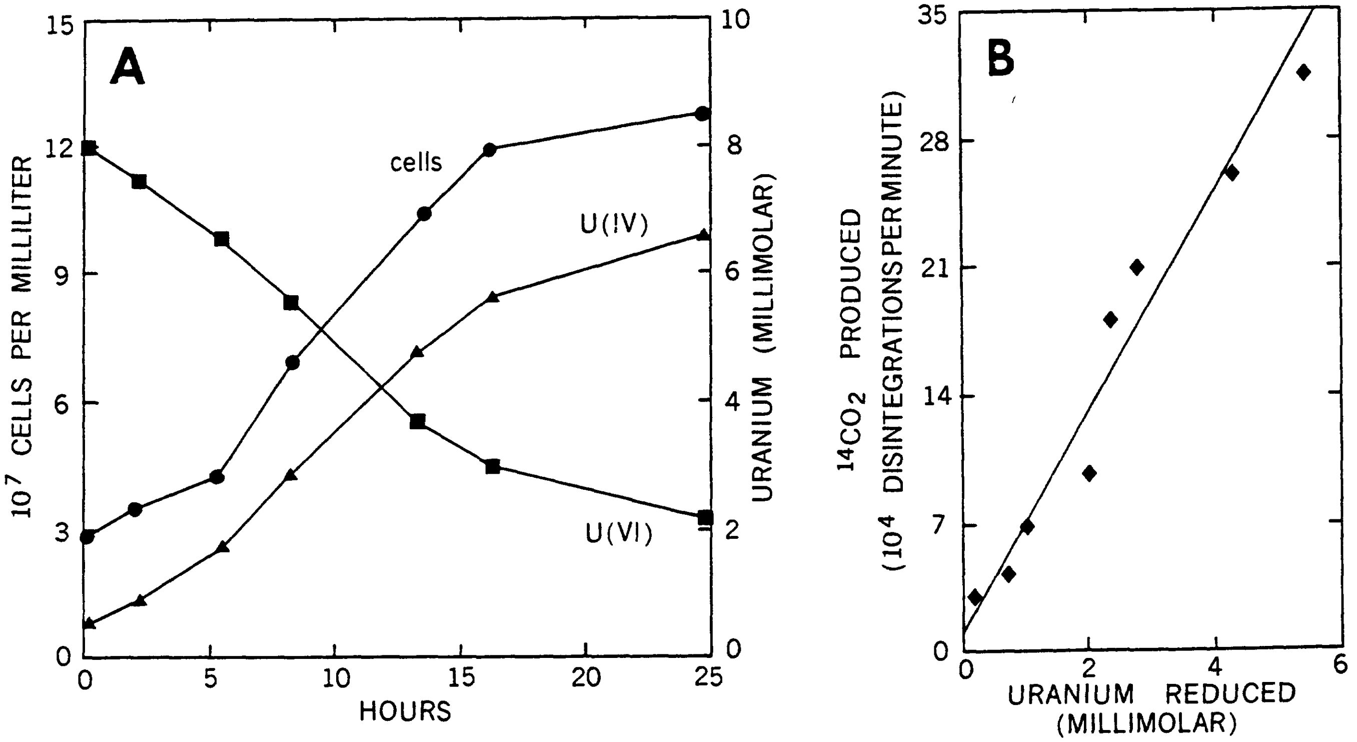

Figure 1. Growth of GS-15 with U(VI) reduction (A) and relation between U(VI) reduction and $[2\text{-}^{14}C]$ acetate oxidation during growth (B). In (B), the acetate concentration was 3.5 millimolar, including 0.5 microcuries of $[2\text{-}^{14}C]$-acetate (from Lovley and others, 1991, fig. 1).

and U(VI) was rapidly reduced in cell suspensions that had been repeatedly washed and resuspended in iron-free buffer.

One other organism, *Shewanella putrefaciens*, is known to obtain energy for growth from electron transport to Fe(III) (Myers and Nealson, 1988; Lovley and others, 1989). *S. putrefaciens* grew with H_2 as the sole electron donor and U(VI) as the electron acceptor (fig. 2). In parallel studies, the stoichiometry of H_2 consumption and U(VI) reduction was consistent with the reaction

$$H_2 + U(VI) \rightarrow U(IV) + 2H^+$$

Other electron donors for Fe(III) reduction by *S. putrefaciens* (formate, lactate, pyruvate) also supported U(VI) reduction. Cell suspensions of the sulfate-reducing microorganism, *Desulfovibrio desulfuricans* also reduced U(VI) at rates comparable to those for GS-15 and *S. putrefaciens* (data not shown). Studies on U(VI) reduction with killed controls and temperature optima studies indicated that U(VI) reduction by *D. desulfuricans* was an enzymatic reaction. However, in contrast to the results with GS-15 and *S. putrefaciens*, *D. desulfuricans* could not grow in a medium with U(VI) as the sole electron acceptor.

Neither H_2 nor any of the organic electron donors for U(VI) reduction by GS-15 or *S. putrefaciens* reduced U(VI) in the absence of the organisms (fig. 3 and data not shown). Furthermore, reduction of U(VI) in washed cell suspensions of GS-15 or *S. putrefaciens* was much faster than the reduction of U(VI) in the presence of a high concentration (1 millimolar) of sulfide (fig. 3). With extended incubation cell suspensions of GS-15 reduced U(VI) concentrations below 0.4 micromolar.

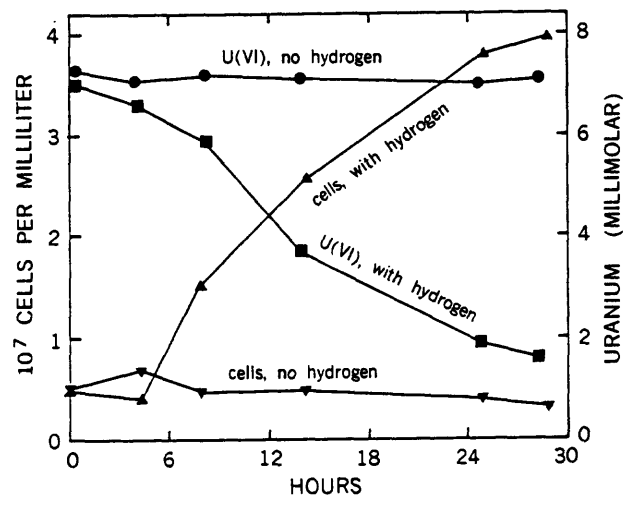

Figure 2. Growth of *S. putrefaciens* with U(VI) reduction with H_2 as the electron donor. Controls had no added H_2 (from Lovley and others, 1991, fig. 2).

These results demonstrate that, although abiological reduction of U(VI) by sulfide, H_2, or organic compounds is typically considered to be the mechanism for U(VI) reduction in sedimentary environments (Jensen, 1958; Hostetler and Garrels, 1962; Langmuir, 1978; Maynard, 1983), enzymatic reduction of U(VI) by microorganisms using U(VI) as a terminal electron acceptor is also possible. Furthermore, microbial reduction of U(VI) has the potential to proceed much

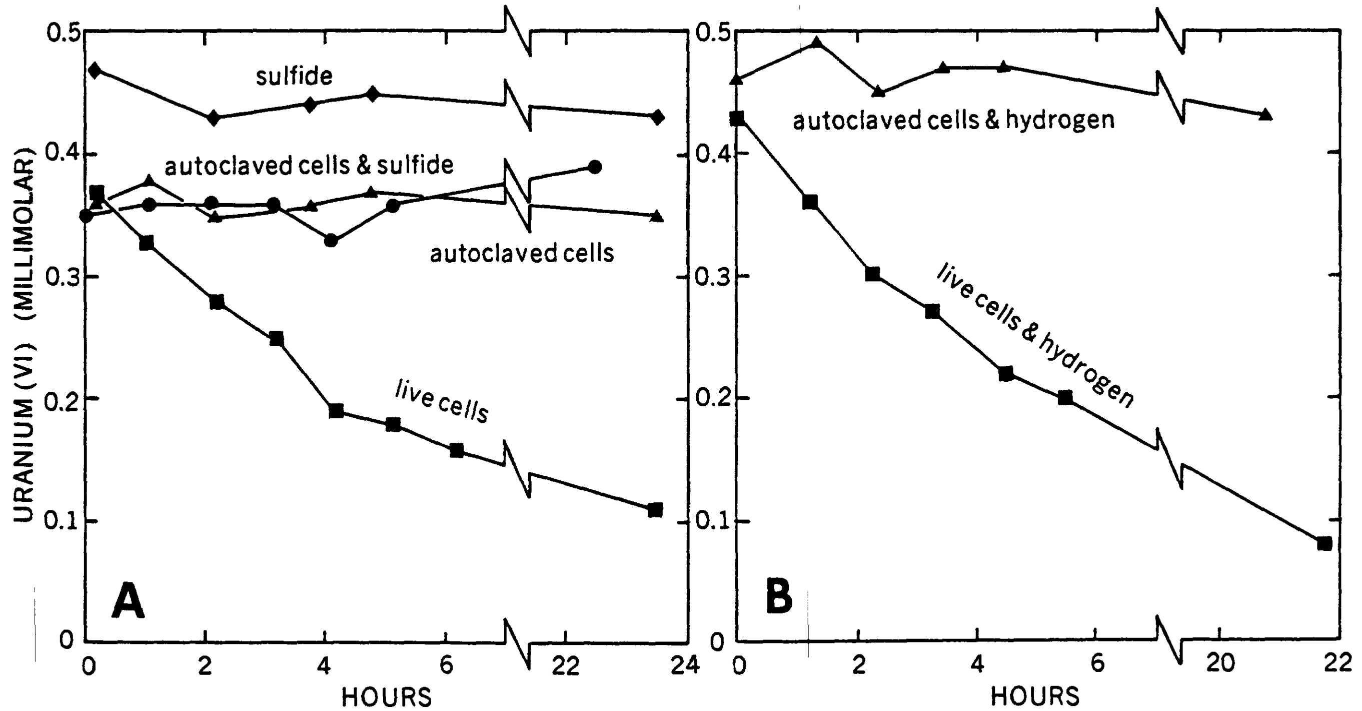

Figure 3. Biological versus abiological U(VI) reduction in washed cell suspensions of GS-15 (A) or *A.putrefaciens* (B) (from Lovley and others, 1991, fig. 3).

more rapidly than abiological U(VI) reduction. Prior evidence for the potential of microorganisms to reduce U(VI) was the report that, in the presence of U(VI), crude cell-free extracts of *Micrococcus lactilyticus* consumed H_2 in quantities that were consistent with U(VI) reduction to U(IV) (Woolfolk and Whiteley, 1962). However, these extracts reduced a wide range of metals with no evidence that the metal reduction was an enzymatic reaction or had any physiological significance in whole cells (Ghiorse, 1988).

The relative potential for microbiological and abiological U(VI) reduction in reduced sediments, was further evaluated by adding U(VI) to highly reduced methane-producing, sulfide-containing, sediments of the Potomac River (fig. 4). U(VI) reduction was much more rapid and extensive in the biologically active sediments than in sediments in which the microorganisms were inactivated with heat. The microorganisms responsible for the U(VI) reduction were not identified, but these sediments do contain Fe(III)-reducing microorganisms that rapidly become active when an electron acceptor is added (Lovley and Phillips, 1987). These results further suggest that models for U(IV) deposition in sedimentary environments need to consider the possibility that microbial populations that have grown up with Fe(III), or possibly other electron acceptors, can reduce U(VI) entering these environments.

The potential for uranium contamination of surface and ground waters through uranium mining activities, irrigation of agricultural lands, and disposal of nuclear wastes is an environmental concern. The results presented here suggest that, in many instances, it may be possible to immobilize uranium contamination by stimulating microbial U(VI) reduction in aquatic sediments or ground water. GS-15 and other Fe(III)-reducing microorganisms can oxidize important organic contaminants with Fe(III) as the electron acceptor (Lovley and others, 1989; Lovley and Lonergan, 1990). Thus, in the case of "mixed wastes" that contain organic contaminants and radioactive metals, the activity of U(VI)-reducing bacteria might be able to couple the decomposition of toxic organic compounds with the immobilization of uranium. Other radioactive metals, such as plutonium and technetium that have multiple redox states and are insoluble in the reduced form, could potentially be treated in a similar manner.

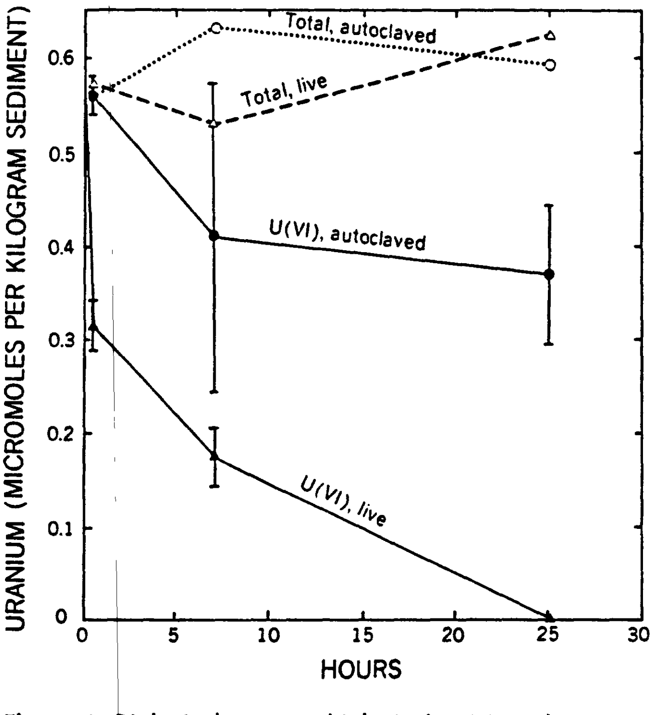

Figure 4. Biological versus abiological U(VI) reduction in anaerobic sediments from the Potomac River. Sediments were sterilized by autoclaving (121 °C. 1 hour) on 4 consecutive days (from Lovley and others, 1991, fig. 4).

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MAPPING SUBSURFACE ORGANIC COMPOUNDS NONINVASIVELY BY THEIR REACTIONS WITH CLAYS

By Gary R. Olhoeft[1] *and* Trude V. V. King[1]

ABSTRACT

One of the most difficult tasks at hazardous waste sites is the mapping of organic contamination. The geophysical technique, complex resistivity, has been shown to be useful for mapping some organics through their reactions with clay minerals, although the processes being observed are commonly unknown. Laboratory evidence indicates that toluene in contact with montmorillonite is physically adsorbed onto the surface of the clay, coordinating with the exchangeable cations on the clay surface, becoming a cationic radical, and polymerizing in the vicinity of the Lewis Acid surface of the clay. This clay-catalyzed polymerization is consistent with known data from polymer chemistry and the electrochemistry of the cationic polymerization of toluene. These laboratory results explain the field data from the Willow Springs hazardous waste site, Calcasieu Parrish, Louisiana, and demonstrate that complex resistivity measurements can map the presence of toluene (where it is in contact with clay) noninvasively through the electrochemical signature of the montmorillonite-toluene polymerization.

INTRODUCTION

Invasive site characterization investigations, such as drilling, provide detailed information about very localized spots at a site, with increased potential for release or spread of contaminants. Surface geophysical techniques can aid in the investigation of hazardous waste sites by providing continuous information about physical and chemical properties in the earth in both areal and depth extent, noninvasively, remotely, safely, and inexpensively (Olhoeft, 1986, 1988; Walther and others, 1986).

Problems associated with contamination of the environment by organic compounds are among the most difficult to resolve. Locating the movement of subsurface contaminant plumes to delineate inorganic chemical contamination at a site is relatively easy, but it can be exceedingly difficult for organic chemicals. Olhoeft (1986) describes case histories where geophysical methods were used to locate inorganic and organic contaminants at several sites. Complex resistivity was demonstrated as one technique to map contamination by organic compounds through the electrochemical signature of clay-organic chemical reactions. At the time that paper was written, the details of the clay-organic interactions were not understood. Which organic chemicals will react with clays (some do not) are still not fully documented, and not all observed clay-organic reactions are understood (Fitch, 1990; Lucius and others, 1990).

The movement of organic solvents through the soil column is a complex process dependent on factors such as aqueous solubility, chemical and biological activity, and degree of interaction with soil particles (Mortland, 1970; Burchill and others, 1981; Bolt and Van Riemsdijk, 1987; Raussell-Colom and Serratosa, 1987; Westall, 1987; Dragun, 1988; Sawhney and Brown, 1989). It is the interaction of organics with soil, especially clay minerals, that appears to cause the electrochemical process that is measured by the complex resistivity technique. These reactions between organics and clays are important to observe, not only to locate organic plumes in the subsurface, but also because they commonly indicate modification of the clays. Most organics that react with clays cause large increases in hydraulic conductivity (see discussion in Theng, 1979, and summary in Dragun, 1988), limiting the effectiveness of clays as barriers.

LABORATORY MEASUREMENTS ON FIELD CORES

Complex resistivity is a geophysical method similar to electrochemical impedance spectroscopy (Sluyters-Rehbach and Sluyters, 1984; Olhoeft, 1985) that allows study of chemical processes in the laboratory or in the field (from the surface of the earth or in boreholes). Both techniques involve the passage of an electric current through a material, and the measurement of the electric voltage generated by the resistance to that current flow. The ratio of the voltage response to the current stimulus is called impedance. Measured at finite frequencies, there is an observable shift in time between the stimulus and the response. The voltage:current amplitude ratio is the magnitude, and the time shift is the phase of a complex impedance. This complex impedance is normalized by the measurement geometry to become complex resistivity. The measurement and data analysis procedures described in Olhoeft (1985) were used to acquire the complex resistivity spectra. The detailed treatment of the samples and data are given in Olhoeft (1985, 1986).

Figure 1 shows the laboratory complex resistivity measurements on core from two wells at the waste disposal facility in Willow Springs, Calcasieu Parrish, La. Core from well Cu-875 (designated MW-22 in earlier reports) is uncontaminated, and core from well Cu-881 (MW-27) is contaminated by organic compounds. The contamination results from the disposal of petrochemical wastes and oil field brines in unlined lagoons (D.A. Trudeau, J.S. Hanor, G.R. Olhoeft and others, U.S. Geological survey, written commun., 1988). The relatively frequency-independent resistivity, small phase angles, low Hilbert distortion, and low total harmonic distortions for the uncontaminated core from well Cu-875 indicate a physical mixture of materials without any significant chemical reactivity. The strongly frequency dependent resistivity, high phase angle (especially near 100 Hz (hertz)), and increased nonlinear distortions (both Hilbert and total harmonic) indicate a strongly chemically

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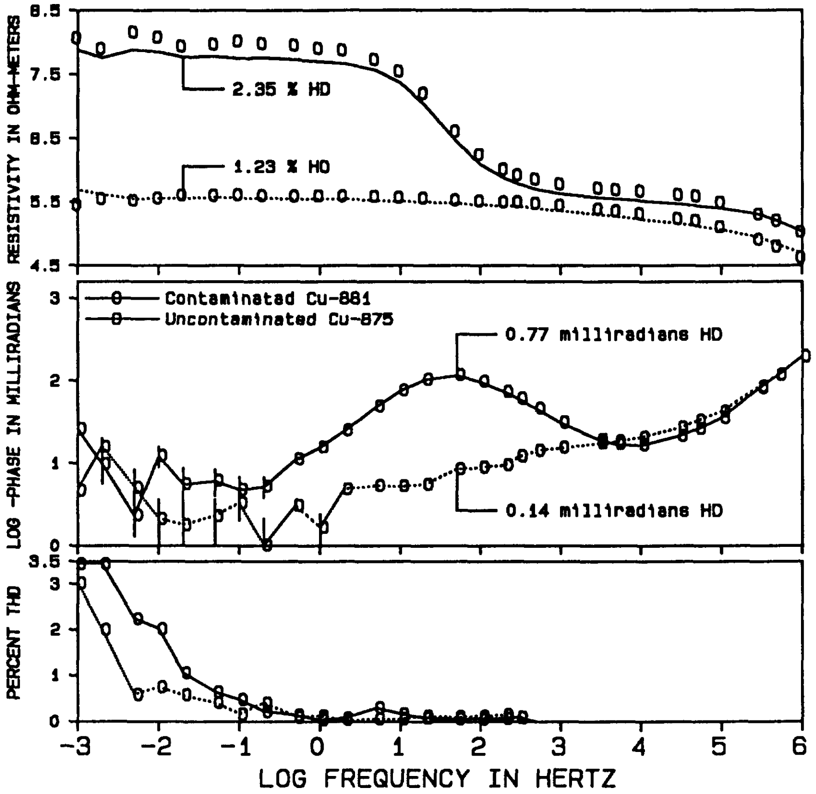

Figure 1. The complex resistivity spectra of core samples from an uncontaminated well (well Cu-875, solid line) and a contaminated well (well Cu-881, dashed line) (modified from Olhoeft, 1985). The contaminated sample is from near the source disposal lagoon (D.A. Trudeau, J.S. Hanor, G.R. Olhoeft, and others, U.S. Geological Survey, written commun., 1988). The increased frequency dependence of resistivity, increased phase, increased Hilbert distortion (HD), and increased total harmonic distortion (THD) indicate increased chemical reactivity.

reacting mixture in the contaminated core from well Cu-881. When originally measured, the reason for the difference between the complex resistivity measurements of uncontaminated and contaminated cores was not known. However, the difference was so pronounced as to be immediately exploitable by field measurements.

FIELD MEASUREMENTS

Figures 2 and 3 illustrate part of the geophysical field data acquired at the waste disposal facility in Willow Springs, Calcasieu Parrish, La. (the remainder of the data is in D.A. Trudeau, J.S. Hanor, G.R. Olhoeft and others, U.S. Geological Survey, written commun., 1988). The electrical conductivity data mapped in figure 2 was performed with a Geonics[2] EM-34 electromagnetic induction instrument with a 20-m (meter) coil spacing and vertical coil orientation. The conductivity is the reciprocal of the resistivity. The complex resistivity measurements agreed with the electromagnetic induction measurements where the two overlapped. However, the electromagnetic measurements are more extensive because the site operator forbade site access with the complex resistivity equipment. The conductivity map clearly shows the plume of inorganic contaminants that results from the disposal of brines.

The complex resistivity field data were acquired using the same measurement apparatus as the laboratory core (Olhoeft, 1985), but using a Wenner electrode array to contact the ground. Figure 3 shows the corresponding complex resistivity phase data map from the 10-m a-spacing, Wenner array, plotted as the difference between the 10 and 0.01 Hz phase measurements. The difference was plotted to normalize out the background variability in the natural soils; 0.01 Hz was the lowest field frequency measured, and 10 Hz was a compromise between observation of the chemical reaction phase peak and higher frequency inductive coupling effects. No data were collected within the fence site because of access restrictions noted above. The phase-difference map clearly shows the activity of the chemical process associated with the clay-organic reaction.

LABORATORY MEASUREMENTS ON SYNTHETIC CLAY-TOLUENE MIXTURES

Figure 4 shows the complex resistivity (electrochemical impedance) spectra of montmorillonite-toluene mixtures (data from Sadowski, 1988). The prominent relaxation feature centered near 100 Hz is present in water-montmorillonite-toluene mixtures, but it is not present in the wet clay alone (when either water or toluene wet). This relaxation feature is

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[2] The use of brand, firm, or trade names in this paper is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

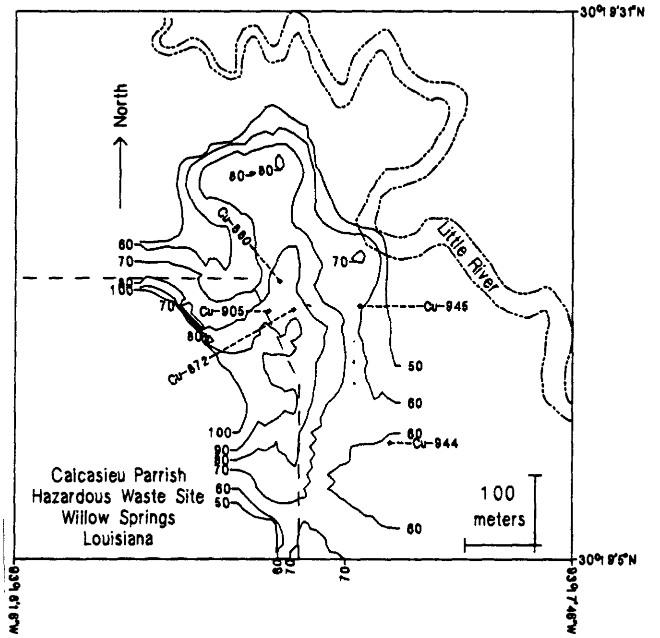

Figure 2. Contours of electrical conductivity (in millimhos per meter) measured with an electromagnetic induction instrument at the waste disposal facility in Willow Springs, Calcasieu Parrish, Louisiana (from G.R. Olhoeft, J.E., Capron, and J.E. Lucius, U.S. Geological Survey, written commun., 1988).

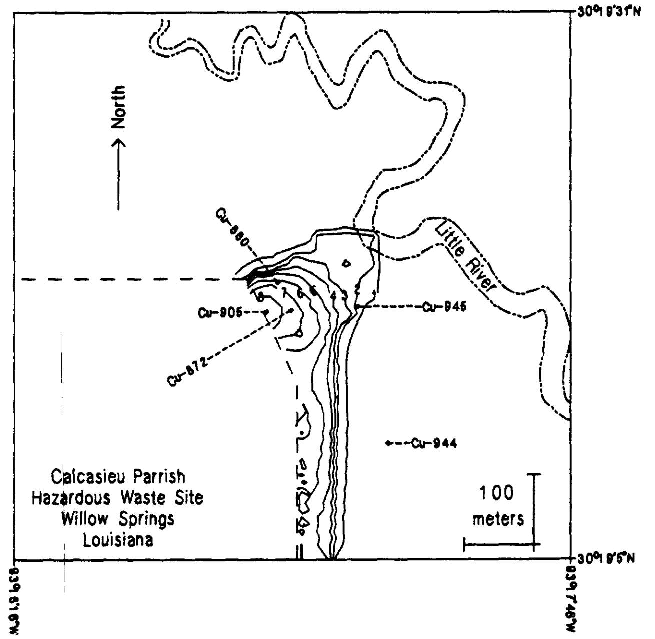

Figure 3. Contours of the difference between 10 and 0.01 hertz phase (in milliradians) measured with the complex resistivity technique at the waste disposal facility in Willow Springs, Calcasieu Parrish, Louisiana (from G.R. Olhoeft, J.E.. Capron, and J.E. Lucius, U.S. Geological Survey, written commun., 1988).

very similar to the one observed by Olhoeft (1986, fig. 1) in contaminated core samples from a landfill used for the disposal of petroleum brines. Figure 5 overlaps the laboratory complex resistivity spectra from montmorillonite-water mixtures with and without toluene (Sadowski, 1988) with the similar spectra from clean and contaminated core (fig. 1). It is remarkable that the montmorillonite clay and montmorillonitic soil core are similar (from Wyoming and Louisiana) when both are clean and contaminated by toluene.

Relaxation features, such as those shown in the complex resistivity spectra of figures 4 and 5, may be caused by physical or chemical relaxation phenomena related to charge transport and polarization. The increase in resistivity at low frequency with increasing toluene concentration reflects the changes in charge transport caused by volumetric physical mixing of a more resistive material (toluene) into a more conductive material (wet clay). The increasing phase near 100 Hz reflects increased polarization with increasing toluene concentration. The shape of the frequency dependence of resistivity and phase around 100 Hz indicates a relaxation process. Such a relaxation process is indicative of the separation of charge (polarization) that occurs during chemial reactions. The frequency of the phase peak may be used to determine the scale length of the process (if diffusion limited) or the speed (if kinetics or reaction rate limited).

Pinnavaia and others (1974) have observed the formation of an unidentified polymer when toluene is adsorbed onto the surface of Fe^{3+}- or Cu^{3+}-montmorillonite. Such polymer formation from the mixing of simple organics with clay minerals is frequently noted in the literature but little understood (Theng, 1974, 1979; Rupert and others, 1987; Dragun, 1988; Gibbons and Soundararajan, 1988, 1989). The formation of a polymer from toluene catalyzed on the surface of montmorillonite may explain the observed relaxation near 100 Hz in the complex resistivity spectra.

The polymerization of toluene is explained electrochemically as the oxidative coupling of alkylbenzenes to bibenzyls (Parker and Burgert, 1968; Anderson and Stocker, 1983) or poly(*p*-phenylenes) (Stevens, 1975) or other polymers (Tomilov and others, 1972), and then continued oxidation of the intermediate cationic radicals to successively higher molecular weight polymers. In some studies, the reactions were found to be kinetics limited with rate constants on the order of 100 to 870 s^{-1} (Clarke and others, 1976; Bewick and others, 1980). Such rates are consistent with an observed relaxation peak near 100 Hz as in figures 4 and 5.

However, the process of oxidation and polymerization also has been observed to be diffusion limited for organics with limited solubility in water (such as toluene), requiring the presence of a catalyst and reactive intermediates (Gourcy and others, 1979; Rudd and Conway, 1983). The surface of montmorillonite behaves like the Lewis Acid catalyst (Mortland and Raman, 1968; Solomon, 1968; Rupert and others, 1987) required for the toluene oxidizing polymerization reaction (Stevens, 1975; Dragun and Helling, 1985; Reichardt, 1988). The reaction process involves several intermediate steps and is probably similar to that described by Osa and others (1969) for oxidation and cationic polymerization of benzene (see also Kovacic and Koch, 1969; Stevens, 1975; Mortland and Halloran, 1976; Bowden, 1979; Dragun and Helling, 1985; Dragun, 1988, p. 307; Walter and others, 1990). Gandini and Cheradme (1985) note that the addition of the methyl group enhances

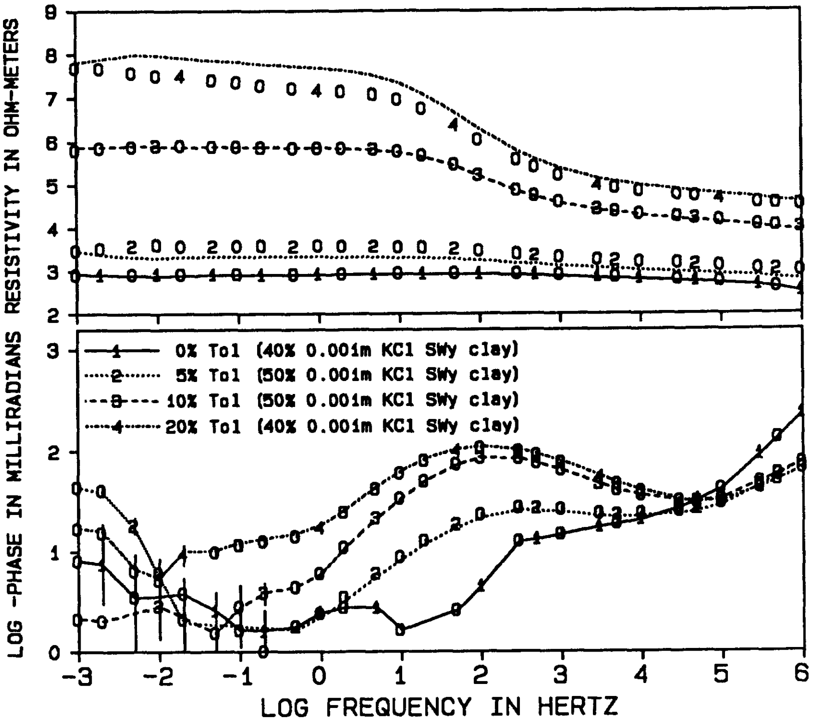

Figure 4. The complex resistivity (electrochemical impedance) spectra of SWy-1 montmorillonite mixed with 0.001 m (molar) KCl aqueous solution and toluene (Tol) from data in Sadowski (1988). The plotted symbols are data points and the lines are a fitted test for determination of Hilbert distortion and relaxation time constant distribution (see Olhoeft, 1985). Vertical error bars are shown where errors are greater than the size of the data plotting symbol.

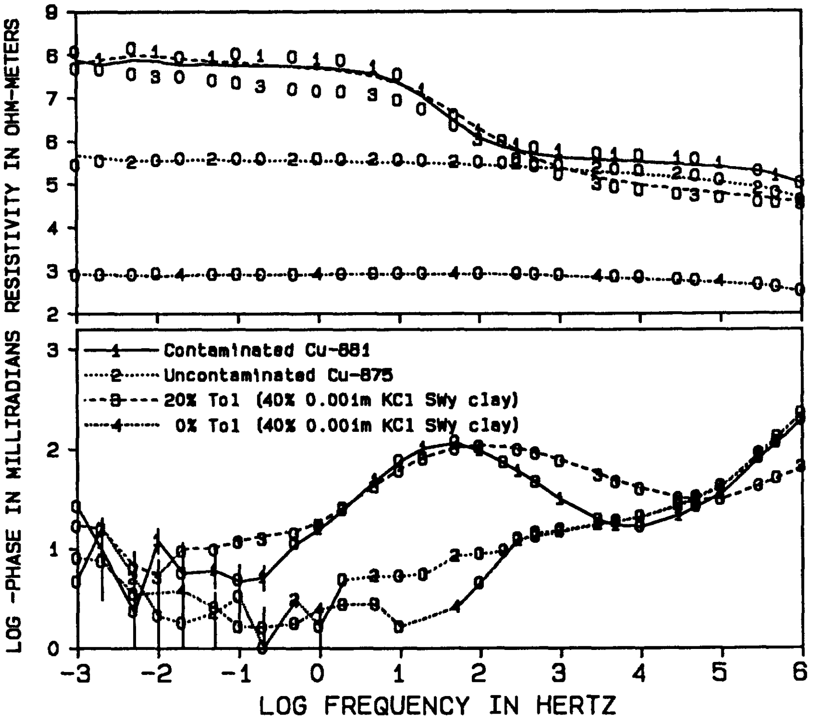

Figure 5. Complex resistivity measurements of the mixture of 20 weight percent toluene in montmorillonite (from curve 4 in fig. 4) compared to measurements of the core sample from near the source of contaminant disposal at the Willow Springs, Calcasieu Parrish, Louisiana, waste disposal site (fig. 1).

polymerization of toluene compared to benzene. For toluene on montmorillonite, this process eventually (over a period of hundreds of seconds) results in a polymer interconnection between the montmorillonite platelets (see the discussion of aggregation and flocculation in Theng, 1979; Burchill and others, 1981). Montmorillonite-water gels normally exhibit scale ordering on the order of a few to tens of micrometers (Greenland and Hayes, 1978; Theng, 1979). If the process behind the observed complex resistivity relaxation is diffusion-limited polymerization, the 100 Hz relaxation suggests the result of this process is the interconnection of the platelets on a scale of about a hundred micrometers (see Burchill and others, 1981).

On the basis of the infrared spectra of the clay-toluene and clay-toluene-water mixtures (King and Olhoeft, 1989), it appears that the toluene is interacting with the clay by a combination of physical adsorption and complexation, followed by polymerization. Mortland and Pinnavaia (1971) and Pinnavaia and others (1974) discuss interactions between alkyl-substituted benzenes and copper substituted clays and classified the complex interaction as type I. In type I interactions, the benzene ring remains planar and retains its aromaticity. Observed infrared vibrational frequencies show marked shifts relative to liquid toluene. In type II interactions, the physically adsorbed toluene shows smaller frequency shifts relative to liquid toluene (Pinnavaia and others, 1974). The failure to form type II complexes in toluene-Fe^{3+}-hectorite mixtures is explained by the polymerization or oligomerization on the interlamellar surface of the mineral (Pinnavaia and others, 1974). The single band in toluene at 2,870 cm^{-1} was observed (King and Olhoeft, 1989) to split into two bands at 2,873 and 2,855 cm^{-1} when the toluene is mixed with montmorillonite. The 2,873 cm^{-1} is the 2,870 cm^{-1} band shifted due to adsorption of the toluene onto the montmorillonite. The new 2,855 cm^{-1} band is interpreted to result from the polymer bibenzyl formed by the interaction of toluene with montmorillonite. Polyphenylenes are another possible interpretation (Simons, 1978); however, inadequate standard reference spectra preclude definitive interpretation of the polymer.

CONCLUSIONS

The spectroscopic evidence (Pinnavaia and others, 1974; Theng, 1974; King and Olhoeft, 1989; Walter and others, 1990) indicate that toluene in contact with montmorillonite first physically adsorbs onto the surface of the clay and coordinates to the exchangeable cations on the clay surface. The cation- coordinated toluene complex loses a proton to become a cationic radical (as in Osa and others, 1969). The electrochemical evidence (Nyberg, 1978; Eberson and Utley, 1983a,b) indicates that this adsorption and radical formation occurs rapidly (microseconds or less). Both the physically adsorbed and coordinated toluene forms are single-layer intercalation complexes (see review in Theng, 1974).

The coordinated toluene radical is in the vicinity of the Lewis Acid surface of montmorillonite that catalyzes polymerization. The polymerization proceeds as oxidative coupling of methylbenzene (toluene) to bibenzyls (Parker and Burgert, 1968; Tomilov and others, 1972; Anderson and Stocker, 1983) or poly(*p*-phenylenes) (Kovacic and Koch, 1969; Stevens, 1975) and then of the intermediate cationic radicals to successively higher molecular weight polymers. This process is the clay-catalyzed (Dragun and Helling, 1985) equivalent of the electrochemical sequence described by Osa and others (1969) and Tomilov and others (1972). Different electrochemical studies (see discussion above) indicate the polymerization may be either diffusion limited or kinetic limited. In either case, the rate of polymerization is consistent with the relaxation process observed by the complex resistivity measurements. The long-term limiting case, however, should be the diffusion limited relaxation of polymer-interconnected clay platelets as the clay surfaces become completely covered by adsorbed toluene or polymer. The infrared spectroscopic evidence for polymerization is suggestive of this process, but inconclusive because of the inadequacy of reference standard spectra for the possible polymer products.

Measurement of complex resistivity magnitude is related to volume effects (charge transport). Measurement of complex resistivity phase is related to surface concentration and processes (charge separation or polarization). Thus, the phase is a much more sensitive indicator of organic contamination than is the magnitude (fig. 4). On the basis of field data reported in Olhoeft (1986), D.A. Trudeau, J.S. Hanor, and G.R. Olhoeft, U.S. Geological Survey, (written commun., 1988), and summarized here in figures 2 and 3, complex resistivity from the surface of the ground can noninvasively map the presence of toluene by exploiting the electrochemical signature of the montmorillonite-toluene polymerization process at concentrations of a few percent to depths of several meters. Similar reactions need investigation for other clay-organic mixtures (Isaacson and Sawhney, 1983; Inoue and Yoneyama, 1987; Fitch, 1990; Lucius and others, 1990).

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AN AUTOMATED METHOD TO QUANTIFY PHYSICAL BASIN CHARACTERISTICS

By James J. Majure[1] *and* David A. Eash[1]

ABSTRACT

A method has been developed to automate the process of quantifying physical basin characteristics. This method will be used to quantify physical basin characteristics for correlation with surface-water quality within drainage basins. The method employs a combination of two software packages. The first package processes digital elevation data for the land surface and generates three geographic information system data sets for a basin representing (1) the drainage network, (2) elevation contours, and (3) the surface-water drainage divide. The second package is a set of programs that quantifies 27 basin characteristics from the three previously generated geographic information system data sets.

In order to evaluate the accuracy and efficiency of the automated method, comparison data sets are being generated by two additional measurement methods at three different map scales. Preliminary comparisons with basin characteristics generated from manual measurements indicate that, with a few exceptions, the automated method can produce reliable results. Limitations inherent to the scale of the digital elevation data appear to account for most of the differences in the quantifications generated using the automated method. The automated method provides a significant reduction in the time required to quantify physical basin characteristics.

INTRODUCTION

Physical basin characteristics are a major influence on the flow of water within a drainage basin. Because of this, these characteristics also play an important role in the surface-water transport of nonpoint-source contaminants within a drainage network. An effective method of quantifying basin characteristics would make it possible to relate water quality to basin characteristics for large areas, possibly providing an improved understanding of the effect of physical basin characteristics on surface-water quality in a basin.

In the past, quantification of physical basin characteristics was a tedious and time-consuming process. With the advent of geographic information systems (GIS), the quantification process has been simplified. However, the entry of drainage-basin data onto the system is still a tedious task. A method has been developed to automate the process of data entry and quantification of physical basin characteristics.

The method that has been developed employs a combination of two existing software packages. The first package is a set of Fortran programs that processes digital elevation model (DEM) data, producing three ARC/INFO[2] coverages that represent selected aspects of a drainage basin. The coverages generated for each basin include (1) the drainage network, (2) elevation contours, and (3) the surface-water drainage divide. The second package is a set of ARC Macro Language (AML) and INFO programs that quantify basin characteristics from the three previously generated ARC/INFO coverages.

In order to verify the accuracy of the automated quantifications, comparison data sets are being generated by two additional measurement methods and three different map scales. These comparison data sets are also being used to test for map-scale dependency.

This paper describes the automated method that was developed to quantify physical basin characteristics, and provides a summary of the quantification results obtained in the testing of comparison data sets.

PROCEDURES

Several processing steps are necessary for the application of each of the two software packages used in the automated method of quantifying basin characteristics. The procedures for each package are discussed in detail in the following sections of the paper.

Digital Elevation Model Processing

The first software package is a set of Fortran programs that process DEM data, producing three ARC/INFO coverages that are a digital representation of selected aspects of a drainage basin. This software was developed by Jenson and Dominque (1988) of the U.S. Geological Survey, Eros Data Center (EDC). The EDC software processes a DEM file, creating several output files that are converted into ARC/INFO coverages. Several additional Fortran programs have been written to carry out this conversion process. The EDC and conversion programs are all driven by a set of Prime Command Processor Language (CPL) and ARC AML programs. This provides a consistent user interface. The CPL and AML programs each carry out several processing steps, and enforce a naming convention that allows the user to enter a single name for each data set being processed. The AML programs allow programs to be executed from within ARC's Arcplot subsystem and the results immediately plotted to the screen.

To begin DEM processing, a CPL program is executed, which, in turn, executes several EDC programs that produce four files: (1) a processed DEM file called a LEV file; (2) a flow direction (DIR) file, each cell of which indicates the direction water flows from the cell; (3) a count (CNT) file, each cell of which indicates the total number of

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[1] U.S. Geological Survey, Iowa City, Iowa

[2] The use of brand names in this paper is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

cells that drain into it, and (4) a delta (DLT) file, each cell of which indicates the difference between the CNT file value of the cell it flows into and its CNT file value. After this initial step is complete, these files are processed and converted into ARC/INFO coverages by the following AML programs executed in Arcplot.

- The first AML program generates the drainage-network coverage. This AML executes a program that reads the CNT and DIR files and creates a drainage-network file in ARC's GENERATE format.This file is then read into an ARC/ INFO coverage (fig. 1a). A threshold can be set to control the frequency of the drainage network.

- The second AML program generates the coverage of elevation contours. This AML executes a program that converts the LEV file into ARC's Single Variable File (SVF) format. ARC programs are then executed to convert the ARC SVF file into an ARC/INFO coverage containing the elevation contours (fig. 1b).

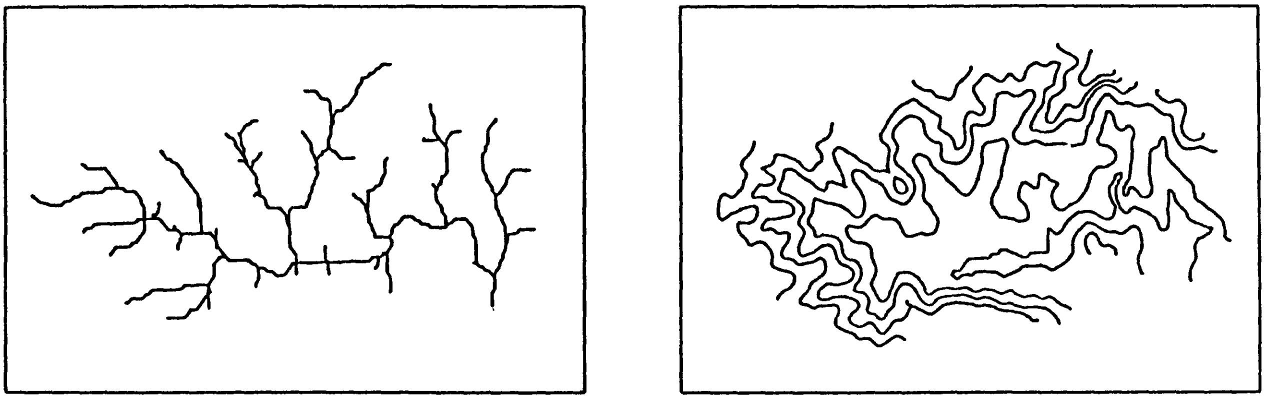
- The third AML program generates the drainage-divide coverage. This AML prompts the user to interactively locate the basin outlet on the drainage network. This point and the DIR file are then used in an EDC program to produce the drainage-divide coverage (fig. 1c).

The three ARC/INFO coverages produced by this step of processing comprise a digital representation of selected aspects of a drainage basin. These coverages are used in the next step of processing to quantify basin characteristics.

Quantification of Basin Characteristics

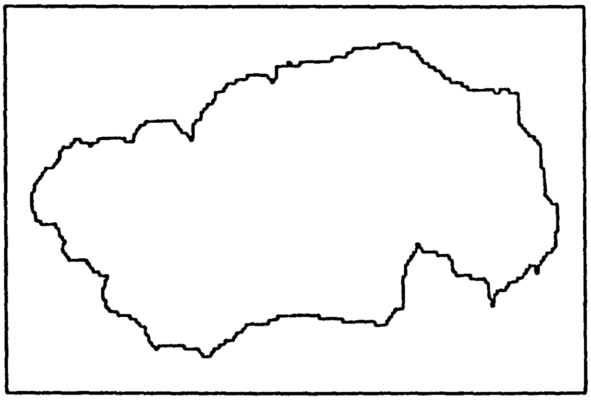
After the three necessary ARC/INFO coverages are generated from the DEM data, basin characteristics are quantified by a set of AML and INFO programs (J.J. Majure and P.J. Soenksen, U.S. Geological Survey, written commun., 1990). These programs process the three coverages shown in figure 1, quantifying the 27 basin characteristics listed in table 1. Eleven of the characteristics are actual measurements made from cartographic data. The remaining characteristics are calculations that make use of these actual-measurement characteristics.

To quantify basin characteristics, attributes must be associated with the arcs and polygons of the three input coverages. These attributes are used by the programs, together with the information automatically maintained by ARC/INFO, such as the length of arcs and the area of polygons, to quantify the basin characteristics. Except for the elevation-contour coverage, the three coverages generated in the first step of processing contain no attributes other than



a) Drainage-network coverage

b) Elevation-contour coverage



c) Drainage-divide coverage

Figure 1. Three coverages comprising a digital representation of selected aspects of a drainage basin.

default system attributes. Therefore, attributes must be added to each of the coverages before basin characteristics can be quantified.

The polygon of the drainage-divide coverage must have the attribute which indicates that it represents contributing drainage area. This is necessary because the programs that quantify basin characteristics allow internal polygons to represent areas of noncontributing drainage area. The programs examine the attributes of any polygons in the drainage-divide coverage to determine the type of area represented by each polygon. With the automated method, however, only one polygon is generated in the drainage-divide coverage, which represents contributing drainage area.

Each arc of the drainage-network coverage must be attributed with its Strahler stream-order number (Strahler, 1952), and with a code indicating whether the arc represents part of the main stream or a secondary stream. Programs have been written to assign the proper stream-order number to each arc and to code those arcs representing the main stream.

The arcs of the elevation-contour coverage are already assigned elevations. The arcs must be identified as being in contributing or noncontributing drainage areas. Because only the contributing area is generated by the automated method, all arcs in the contour coverage are considered to be in contributing drainage areas. Two points are also interactively added to the contour coverage that represent the maximum and minimum elevations of the drainage basin, as determined from a topographic map.

After the necessary attributes are assigned to the three input coverages, basin characteristics can be quantified by executing a single command. This command initiates a separate computation for each of the basin characteristics.

VERIFICATION

In order to verify that the results of the automated method are valid, three data sets are being generated. The data sets are being generated by the following methods:

A. Manual measurements made from 1:24,000, 1:100,00, and 1:250,000 scale topographic maps;
B. Digitized measurements produced by hand digitizing 1:100,000 and 1:250,000 scale topographic maps into ARC/INFO coverages, and processing these coverages using the programs of the second step of the automated method; and
C. Measurements generated from 1:250,000 scale DEM data by the entire automated method.

Three drainage basins, representing small- (21.6 mi^2 (square miles)), intermediate- (182 mi^2), and large- (871 mi^2) sized drainage areas, and different physiographic regions of Iowa, were selected for use in initial data-set comparisons.

Preliminary comparisons at the same map scale for the small- and large-size drainage basins indicate that all of the actual measurement characteristics quantified by method B are within 11 percent of those quantified by method A, with the exception of the main-channel slope. These comparisons indicate that the programs of the second step of the automated method are functioning properly. The problem with the main channel slope appears to be a program error. It is currently being addressed.

A preliminary comparison between characteristics quantified using 1:24,000-scale data by method A and characteristics quantified using 1:250,000-scale DEM data by method C has only been performed for the small drainage basin. The 1:24,000-scale data are being used because they are assumed to be the most accurate quantifications. The density of the drainage network generated by the automated method is calibrated to approximate the drainage network depicted on the 1:24,000-scale topographic maps. The automated method underestimated the basin slope, the main-channel length, and the total stream length, because the 3-arc-second pixel size of the 1:250,000-scale DEM data produce drainage-network and elevation-contour coverages (figs. 1a and 1b) that are more generalized than the drainage network and contours depicted on the 1:24,000-scale topographic maps. The automated method also overestimated the basin perimeter, because the drainage divide generated is a stepped line instead of a smooth line as a result of the raster format of the input DEM data set (fig. 1c). Comparisons for the intermediate and large drainage basins will be completed to verify these findings.

Table 1. Basin characteristics

[Modified from Melton, 1957, Strahler, 1958, and Office of Water-Data Coordination, 1978]

•	TDA	- Total drainage area	•	RR	- Relative relief
•	NCDA	- Noncontributing drainage area	•	MCL	- Main channel length
•	CDA	- Contributing drainage area	•	TSL	- Total stream length
•	BL	- Basin length	•	MCS	- Main channel slope
•	BP	- Basin perimeter	•	MCSR	- Main channel sinuosity ratio
•	BD	- Basin diameter	•	SD	- Stream density
•	BS	- Average basin slope	•	CCM	- Constant of channel maintenance
•	BR	- Basin relief	•	MCSP	- Main channel slope proportion
•	BW	- Effective basin width	•	RN	- Channel ruggedness number
•	SF	- Shape factor	•	SR	- Ratio of main channel slope to basin slope
•	ER	- Elongation ratio	•	FOS	- Number of first-order streams
•	RB	- Rotundity of basin	•	DF	- Drainage frequency
•	CR	- Compactness ratio	•	RSD	- Relative stream density
•	LR	- Lemniscate ratio			

Approximate time required to generate the three different data sets were 16 hours using method A and 1:24,000-scale maps, 13 hours using method B and 1:24,000-scale maps, and 6 hours using method C and 1:250,000-scale DEM data. These time comparisons for the small drainage basin indicate that the automated method provides a significant time reduction in the quantification of physical basin characteristics. Even greater improvements in time reductions are anticipated for larger drainage basins.

SUMMARY

A method has been developed that automates the process of quantifying physical basin characteristics. The method employs a combination of two existing software packages. The first package is a set of Fortran programs that processes DEM data, generating three ARC/INFO coverages that represent a drainage basin. The coverages generated for each basin include (1) the drainage network, (2) elevation contours, and (3) the surface-water drainage divide. The second package is a set of AML and INFO programs that quantify 27 basin characteristics from the three previously generated ARC/INFO coverages.

Preliminary comparisons of basin characteristics generated by the automated method with those calculated from manual measurements indicate that, with a few exceptions, the automated method can produce reliable results. Limitations inherent to the scale of the DEM data may be the cause of differences in the quantifications generated using the automated method. Compared to traditional methods of measurement, the automated method provides a significant time reduction in the quantification of physical basin characteristics.

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THE EFFECT OF SURFACTANTS AND EMULSIONS ON WATER SOLUBILITY OF ORGANIC CONTAMINANTS

By D.E. Kile[1] *and* C.T. Chiou[1]

ABSTRACT

Apparent water solubilities of 1,1-bis(p-chlorophenyl)-2,2,2-trichloroethane 2,4,5,2′,5′-pentachlorobiphenyl, and 1,2,3-trichlorobenzene were determined at room temperature in aqueous solution of linear alkylbenzenesulfonate surfactant and some commercial petroleum sulfonates. Petroleum sulfonates form stable emulsions in water that behave like a bulk organic phase in solubilizing organic solutes. The extent of solubility enhancement is linearly proportional to the concentration of the petroleum sulfonate-oil emulsion, in contrast to a sharp inflection in the vicinity of the critical micelle concentration for a conventional (micelle forming) surfactant. The partition constant of the solute between the petroleum sulfonate oil and water is significantly higher than that between ordinary surfactant monomers below critical micelle concentration and water. When the value is normalized for the nonpolar content of the emulsion, it approximates the solute's octanol-water partition coefficient (K_{OW}). Similarly, the much greater solubility enhancement of solute by linear alkylbenzenesulfonate below the critical micelle concentration than by monomers of conventional surfactants is attributed to a surfactant-oil emulsion formed as a result of the 1.7 percent neutral oil content in commercially formulated linear alkylbenzenesulfonate. These neutral oils are comprised of linear alkylbenzenes and di(alkylphenyl)sulfones. The oil-surfactant emulsion formed constitutes approximately 9 to 10 weight percent of the total linear alkylbenzenesulfonate below critical micelle concentration. Enhancement data for linear alkylbenzenesulfonate above the critical micelle concentration is comparable to those for other surfactant micelles. The data suggest the potential impact of surfactant-emulsion systems at low concentrations on the transport of organic contaminants in the environment.

INTRODUCTION

The transport of an organic contaminant in an aquatic environment depends on its water solubility and its interaction with the sediment phase. Consequently, it is important to consider what factors will influence the water solubility of an organic contaminant. Previous studies have shown that the solubility of relatively insoluble organic compounds can be enhanced by low concentrations of dissolved natural organic matter, such as humic and fulvic acids, through a partition interaction (Chiou and others, 1986, 1987). It is therefore of interest to consider which anthropogenic organic matter introduced into the aquatic environment may exert similar effects. Under this consideration are various organic substances, including widely used commercial surfactants and detergents. The worldwide consumption of surfactants was estimated to exceed 15.5 billion pounds in 1989 (Greek, 1990), and therefore their potential impact resulting from disposal of untreated wastewater may be considerable. Although there is extensive literature regarding solubilization and detergency properties of surfactants, relatively little data have been published concerning their effect on pollutant transport, especially at low concentrations of surfactants.

Surfactants are comprised of three general types of surface-active agents--anionic, cationic, and nonionic--but their product formulations may include additives of nonsurface-active components to give modified detergent characteristics. Conventional (micelle forming) surfactants are molecularly homogeneous and characterized by an amphipathic molecular structure (the molecular species is referred to as monomer) having a polar "head group" and a nonpolar "tail." This structure permits aggregation of surfactant molecules forming nonpolar-interior, polar-exterior aggregates (called micelles) in contact with the aqueous phase when the concentration is raised above a certain point. The concentration above which micelles are formed is called the critical micelle concentration (CMC). The CMC is characterized by a distinct inflection in a plot of the log surface tension as a function of surfactant concentration. Below the CMC conventional surfactants exist as monomers; above the CMC the monomer concentration remains constant at CMC and the amount in excess forms micelles. Because of the large aggregation number of monomers to form micelles, micelles are considered to be a microscopic organic phase. The solubility enhancement of a sparingly soluble solute in surfactant solution thus exhibits an inflection toward much greater enhancement in the vicinity of the CMC, due to micelle formation.

Recent studies on the effects of different classes of surfactants on the apparent water solubility of DDT and 1,2,3-trichlorobenzene (TCB) (Kile and Chiou, 1989) have led to a basic understanding of the impact of conventional surfactants on the transport and fate of organic pollutants. The enhancement effect by monomers is usually weak, especially for ionic surfactants, whereas the effect by micelles approaches that of a bulk solvent. Nonionic surfactants are generally more effective than ionic surfactants because the stronger hydration of the ionic surfactant mitigates the partition interaction with the solute. In solutions of some nonionic surfactants containing a mixture of heterogeneous surface-active agents, the observed nonlinear solubility enhancement of a sparingly soluble compound such as DDT below the CMC is assumed to result from successive micellization of heterogeneous monomers.

Different classes of surfactants yield different results with respect to solubility enhancement. One class of surfactants of special interest is petroleum sulfonates, which are widely used in tertiary oil recovery and ore flotation. These surfactants are composed of surface-active sulfonated alkyl-aryl hydrocarbons and mineral oils that form emulsions in aqueous solution. They are manufactured by treating selected petroleum stocks with sulfuric acid, a process whereby the aromatic components of the petroleum are sulfonated, leaving straight-chain hydrocarbons as free mineral oils. In a strict sense, petroleum sulfonates do not conform to the criteria of "conventional surfactants" because they do not exhibit the monomer-micelle transition due to the presence of oils, but they effectively reduce the surface tension of water as a result of their surface-active sulfonated hydrocarbon components. Because emulsions act as a separate phase even at very low concentrations, they may be expected to show a strong enhancing effect on solute solubility at relatively low concentrations.

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Another class of surfactant of interest is the linear alkylbenzenesulfonate (LAS), the most widely used of the anionic surfactants. This surfactant is prepared commercially by sulfonation of a heterogeneous linear alkylbenzene (LAB) feedstock to a point where approximately 2 percent free (unsulfonated) oil remains; the commercial formulation is therefore composed of heterogeneous sulfonated hydrocarbons (having alkyl chain lengths varying from 12 to 13 carbons and a phenyl ring attached at the 2d to 6th carbon positions) and a small amount of neutral oil. In a sense, LAS represents a hybrid of a conventional surfactant and a petroleum sulfonate, where the heterogeneous alkylbenzenesulfonates exhibit surface-active properties, and the emulsion formed by free oils and surface-active sulfonated hydrocarbons may be expected to exhibit bulk solvent properties that enhance solute solubility below the nominal CMC in a manner similar to that of the petroleum sulfonates.

This paper reports the results of solubility enhancement data of some organic contaminants by these two widely used surfactants and their emulsions on the transport of pollutants in hydrogeological systems.

THEORETICAL CONSIDERATIONS

Surfactants exist as monomers below the CMC. Above the CMC the concentration of monomers remains constant and the micelle concentration is the difference of total concentration and CMC. By treating the micelle as a separate phase (Shinoda and Hutchinson, 1962), the solubility enhancement of a solute by conventional surfactants may be expressed as

$$S_W^*/S_W = 1 + X_{mn}K_{mn} + X_{mc}K_{mc}, \qquad (1)$$

where S_w^* is the apparent water solubility of the solute at surfactant concentration X, with $X = X_{mn} + X_{mc}$; S_w is the intrinsic pure water solubility of the solute; X_{mn} is the concentration of the surfactant monomer; and X_{mc} is the surfactant concentration in micellar form (Kile and Chiou, 1989). The K_{mn} and K_{mc} terms are the partition constants of the solute between the surfactant monomer and the surfactant micelle with water, respectively. This equation gives a general account of the relative contributions of conventional surfactant monomers and micelles to solute solubility enhancement. It predicts an inflection in the plot of the apparent solute solubility as a function of surfactant concentration, showing a straight line with slope = K_{mn} from X = 0 to CMC, and a second line with slope = K_{mc} from $X \geq$ CMC. The considerably greater solvency of the micelle phase compared to that of the monomers suggests a sharp break in this plot in the vicinity of the CMC.

For emulsion systems showing an absence of monomer-micelle transition, the magnitude of solubility enhancement can be accounted for by a single-partition equilibrium of the solute between the emulsified phase and water. The solubility enhancement can be described by

$$S_W^*/S_W = 1 + XK_{em}, \qquad (2)$$

where S_w^* and S_w have the same meanings defined above, X is the concentration of the emulsion, and K_{em} is the partition coefficient of the solute between the emulsified phase and water (Kile and others, 1990). A plot of S_w^* as a function of X gives a linear relation with a slope of S_wK_{em} and an intercept of S_w.

The equations above describe the individual effects of surfactant monomers, micelles, and emulsions on the solubility enhancement of organic pollutants, and serve as a theoretical basis to assess enhancement effects by more complex heterogeneous surfactant systems where emulsions may coexist with surfactant monomers or micelles.

EXPERIMENTAL METHODS

Test solutes were selected to provide a range of pure water solubilities, with extremely insoluble solutes such as DDT expected to give the most sensitive enhancement in the presence of surfactants (Chiou and others, 1986). DDT and TCB were obtained from Aldrich Chemical Co., Inc.[2], and 2,4,5,2',5'-pentachlorobiphenyl (PCB) was obtained from Ultra Scientific. These compounds have a purity of 99 percent or greater and were used as received. Hexane (UV grade) and petroleum ether (high purity) used for extractions were manufactured by American Burdick and Jackson; ethanol, used for neutral oil extraction from LAS, was obtained from USI Chemical Co. Deionized water used for preparing solutions was obtained from a Sybron/Barnstead Nanopure II water treatment system.

Surfactants were obtained either directly from the manufacturer or from a chemical supply company and used without further purification. The petroleum sulfonate surfactants (Petronate L, Petronate HL, Pyronate 40) were obtained from Witco Chemical Corp. These bulk materials are dark brown, highly viscous liquids; their compositions are given in table 1. Stock solutions of the Petronate surfactants at a 5,000 mg/L (milligrams per liter) concentration show a high degree of emulsion (as indicated by light scattering) and are light brown, whereas stock solution of Pyronate 40 at the same concentration is a distinct dark brown and shows less light scattering compared to the Petronate surfactants.

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[2] The use of brand, firm, or trade names in this paper is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

Table 1. *Composition and properties of commercial Petronate and Pyronate surfactants [Source: Witco Chemical Corp.]*

Composition/ Property	Petronate L	Petronate HL	Pyronate 40
Percent petroleum sulfonate:	62	62	41
fraction as hydrocarbon	46.9	48.0	28.6
fraction as $-SO_3Na$	15.1	14.0	12.4
Percent free mineral oil	33.0	32.5	12.0
Percent inorganic salts	.5	.5	8.5
Percent water	4.5	4.5	38.5
Molecular weight of petroleum sulfonate	415-430	440-470	330-350
Percent hydrocarbon in water-free sample[1]	83.7	84.3	66.0

[1] Total of hydrocarbon in petroleum sulfonate and free mineral oil.

LAS was provided by Aldrich Chemical Co., Inc., and Fluka Chemical Corp. as a technical grade powder with a purity (active ingredient) of 80 to 85 percent, with the balance being sodium sulfate. The approximate alkyl-chain distribution according to Aldrich Chemical Co., Inc., is: 5 percent C_{10}, 45 to 50 percent C_{11}, 35 percent C_{12}, 10 to 15 percent C_{13}, and <0.05 percent C_{14}. Results presented have been corrected for purity. Sodium 4-dodecylbenzenesulfonate (4-DBS), a single-molecular component of the commercial LAS formulation, was purchased as a custom-synthesized compound from Aldrich Chemical Co., Inc., with a purity of 98+ percent.

Surface tension was measured using a Fisher Scientific Model 20 tensiometer that operates on the DuNouy principle, by which the force, in dynes per centimeter, necessary to pull a calibrated platinum-iridium ring free of a surface film is measured. Surface tension values at given concentrations were plotted when stable readings were obtained from a series of consecutive measurements. The weight percent of neutral (free) oil in LAS was determined by the American Oil Chemists' Society (AOCS) Official Method Dd 4-60 (Kellenbach and Blank, 1965; American Oil Chemists' Society, 1973). This gravimetric analysis is based on a sequential petroleum ether extraction of an ethanol-water solution of LAS, followed by evaporation of the residual petroleum ether at 60 to 70 °C (degrees Celsius) and a final short drying step near 100 °C. Because of the possibility of loss of volatile low-molecular-weight LAB components during the drying step, the AOCS procedure was modified so that a temperature of ≤ 40 °C was maintained during drying. The neutral oil in LAS obtained by this method was 1.7 percent by weight, corrected for purity of the LAS. The extracted neutral oil was a highly viscous, distinctly yellow liquid that was only sparingly soluble in water. The residual oil-free LAS was recovered as a white powder from the extracted water-ethanol solution by drying under low heat (~50 °C) over a 3- to 4-day period.

Procedures for sample equilibration and solubility determination were the same as described earlier (Chiou and others, 1986; Kile and Chiou, 1989). A series of concentrations was prepared for each surfactant and placed in a 25-milliliter Corex centrifuge tube with Teflon cap liners; the test solute was then added in an amount just sufficient to assure a saturated solution. Triplicate samples were prepared at each concentration, equilibrated on a reciprocating shaker for approximately 48 hours at 24 ± 1 °C, and subsequently centrifuged at 5,000 revolutions per minute (2,987 gravities) for 45 minutes to separate the undissolved solute. Solute particles adhering to the glass walls were carefully removed with a cotton swab, and the meniscus was aspirated to remove suspended particles. This procedure was repeated twice more. An aliquot of supernatant was volumetrically withdrawn and extracted in a volume of hexane required to bring the solute concentration into a detectable range. A pure water blank was run with each sample set as a check on analytical accuracy and completeness of equilibration. The intrinsic water solubilities of DDT, PCB, and TCB at 25 °C are 5.5 μg/L (micrograms per liter), 11 μg/L, and 18 mg/L, respectively; these values are used for subsequent data analyses.

Analysis of DDT and PCB was done by gas chromatography with a cross-linked methyl silicone (0.88-μm (micrometer) film thickness) megabore capillary column (30 m (meter) X 0.53 mm (millimeter)) with a ^{63}Ni electron capture detector. Analysis of TCB was done by gas chromatography using a cross-linked 5 percent phenyl methyl silicone (0.52-μm film thickness) capillary column (25 m X 0.32 mm) and a flame ionization detector.

RESULTS AND DISCUSSION

The compositions of the petroleum sulfonate surfactants (hereafter referred to as PSO emulsions, in contrast to their sulfonated components) are shown in table 1. The heterogeneous mixture, consisting of surface active petroleum sulfonates and free oil, forms a stable emulsion in water. The surface tension plot shown in figure 1 shows a virtually linear relation between log concentration and surface tension indicative of an absence of a monomer-micelle transition. Similarly, corresponding plots of solubility enhancement for DDT (fig. 2) and TCB (fig. 3) are a function of surfactant concentration at room temperature and are linear throughout the range of concentrations studied, in contrast to traditional surfactants that show a sharp break in the vicinity of the CMC (Kile and Chiou, 1989).

Table 2 shows the calculated K_{em} values for DDT and TCB on a water-free, total PSO weight basis. Included in this table for comparison are the partition coefficients for monomers (K_{mn}) and micelles (K_{mc}) for two ionic surfactants, cetyltrimethylammonium bromide (CTAB) and sodium dodecyl sulfate (SDS), and two nonionic surfactants, Triton X-100 and Triton X-114, from an earlier study (Kile and Chiou, 1989). The apparent solubility of DDT at room temperature is shown in figure 2, and corresponding data for TCB are shown in figure 3. Concentrations of PSO used with TCB were higher than those used with DDT to permit greater accuracy in assessing solubility enhancement.

These data show that solubility enhancement of DDT is more than two orders of magnitude greater than that for TCB. These results are consistent with equilibrium partitioning (where the equilibrium partition constant is inversely proportional to the solute's pure water solubility) and are in agreement with the results of an earlier study using natural humic substances (Chiou and others, 1986; 1987). The greater K_{em} values for Petronate L and HL relative to

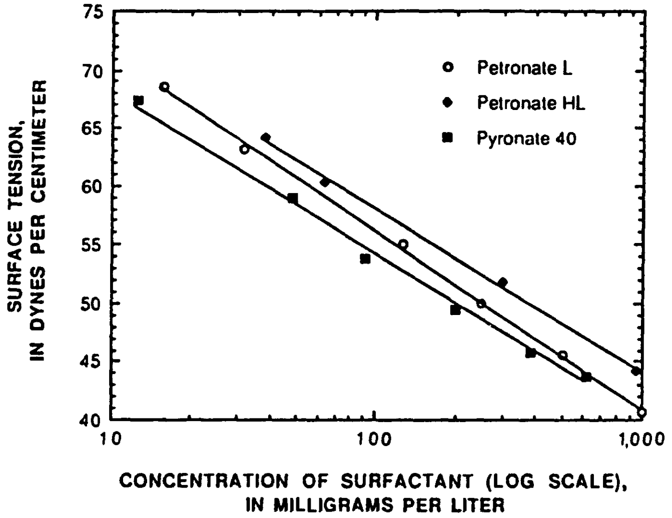

Figure 1. Plot of the surface tension as a function of the logarithm of surfactant concentration for Petronate L, Petronate HL, and Pyronate 40 (modified from Kile and others, 1990, fig. 1; reprinted with permission from Environmental Science and Technology, v. 24, no. 2, 1990. Copyright 1990, American Chemical Society).

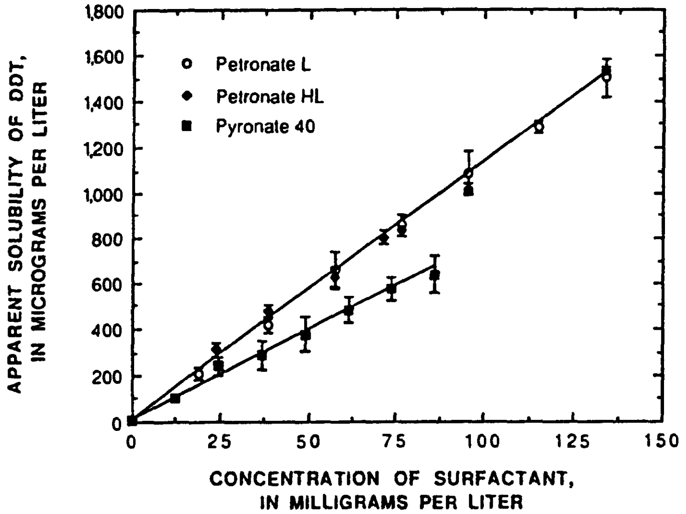

Figure 2. Apparent solubility of DDT in aqueous solution of Petronate L, Petronate HL, and Pyronate 40 (modified from Kile and others, 1990, fig. 2; reprinted with permission from Environmental Science and Technology, v. 24, no. 2, 1990. Copyright 1990, American Chemical Society).

Pyronate 40 are accountable in terms of the higher hydrocarbon content of the former. Normalization of these partition constants on the basis of the nonpolar hydrocarbon content gives K_{em} values of 6.40, 6.39, and 6.32 for Petronate L, HL, and Pyronate 40, respectively. The similarity of these results indicate that solubilization is predominantly effected by the hydrocarbon moiety.

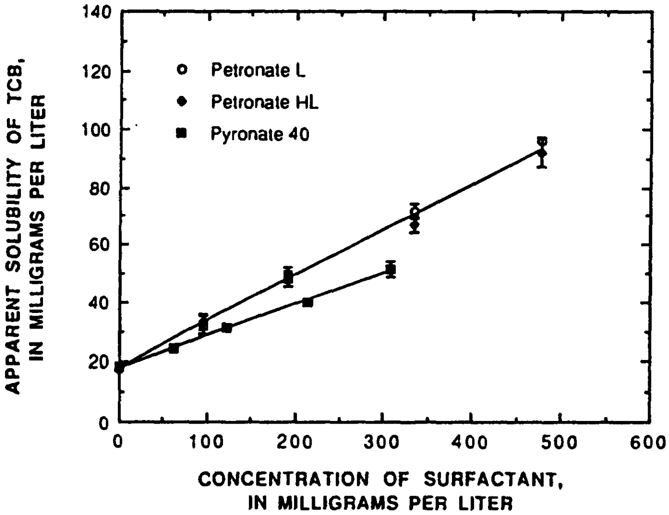

Figure 3. Apparent solubility of 1,2,3-trichlorobenzene in aqueous solution of Petronate L, Petronate HL, and Pyronate 40 (modified from Kile and others, 1990, fig. 3; reprinted with permission from Environmental Science and Technology, v. 24, no. 2, 1990. Copyright 1990, American Chemical Society).

Table 2. *Partition coefficients of solutes with monomers (K_{mn}), micelles (K_{mc}), and emulsions (K_{em}) formed by linear alkylbenzenesulfonate and other surfactants*

Surfactant	1,2,3-TCB	p,p'-DDT	2,4,5,2',5'-PCB
log K_{em}:			
Petronate L[1]	3.94	6.32	-
Petronate HL[1]	3.94	6.32	-
Pyronate 40[1]	3.77	6.14	-
log K_{mn}:			
SDS[2]	ND[3]	2.68	-
CTAB[2]	ND	3.54	-
Triton X-100[2]	ND	4.26	-
Triton X-114[2]	ND	4.59	-
LAS (oil-free)	-	4.08	3.98
4-DBS	-	4.18	-
log K_{mc}:			
SDS[2]	3.54	5.38	-
CTAB[2]	3.80	5.88	-
Triton X-100[2]	3.82	6.15	-
Triton X-114[2]	3.95	6.18	-
LAS	3.69	5.72	5.48
LAS (oil-free)		5.60	5.32

[1] Data from Kile and others, 1990

[2] Data from Kile and Chiou, 1989

[3] ND, not detectable

In comparison to conventional surfactant monomers, PSO emulsions are markedly more effective in enhancing solute solubility; K_{em} values are about 1.5 to 2 orders of magnitude greater than K_{mn} values for the nonionic surfactants (Triton X-100 and Triton X-114), and about 3 orders of magnitude greater than the K_{mn} values for the ionic surfactants (CTAB and SDS). K_{em} values for DDT and TCB are comparable to the K_{mc} values for the nonionic surfactants, but markedly larger than corresponding values for the ionic surfactants, presumably because the ionic hydration sphere of the ionic micelle lowers the overall partition efficiency. The enhancement effect by emulsified PSO systems studied are about 1.5 to 2 orders of magnitude greater than that by aquatic humic and fulvic acids on a total water-free weight basis (Chiou and others, 1986, 1987). A similarity between the K_{em} and octanol-water partition coefficient (K_{ow}) values (log K_{ow} values for DDT and TCB are 6.36 and 4.14, respectively) further substantiates the partition efficiency of the PSO emulsion (Kile and Chiou, 1989). The above data suggest that the emulsified PSO acts like a separate bulk phase at all concentrations; the linear solubility enhancement can be effectively accounted for by equation 2. These results also show that PSO emulsions are much more effective at low concentration than are surfactant monomers or naturally occurring dissolved organic matter.

Although LAS gives a nominal CMC of about 500 mg/L (fig. 4), solubility enhancement studies below the CMC gave anomalous results when compared with traditional surfactant monomers. Figure 5 shows the apparent solubilities of DDT and PCB, respectively, above and below the CMC at room temperature, and figure 6 shows corresponding data for TCB. Solubility data for DDT with LAS obtained from Fluka Chemical Corp., was nearly identical with that of the Aldrich Chemical Co. LAS, and consequently all other studies were made with the Aldrich sample. On one hand, the data showing the monomer-to-micelle transition are consistent with the behavior of a conventional surfactant; two relatively distinct slopes are observed in the vicinity of the measured CMC of the LAS. On the other hand, although the solubility of DDT in above-CMC concentrations of LAS are comparable to that of SDS and CTAB, the magnitude of DDT solubility enhancement by LAS below the CMC is more than 100 times greater than that by SDS and about 30 times greater than that by CTAB. This prominent difference in the below-CMC data suggests that some components of the formulated surfactant influences the degree of solubility enhancement. Commercial LAS contains free oil as a byproduct of the manufacturing process, the free oil being composed of residual LAB and di(alkylphenyl)sulfones formed during sulfonation (Moreno and others, 1988). It is speculated that these oils exist as an emulsion of LAS that is similar to the nature of PSO. To confirm this hypothesis, a comparison is made between the solubility enhancement data of LAS and oil-free LAS.

Removal of the neutral oils of LAS by extraction results in about a tenfold reduction in the apparent solubility of DDT and PCB below the CMC (fig. 7). The oil-free LAS also shows a reduction in the CMC, to about 390 mg/L, as would be expected when a small amount of emulsion suppresses micelle formation in the original LAS solution.

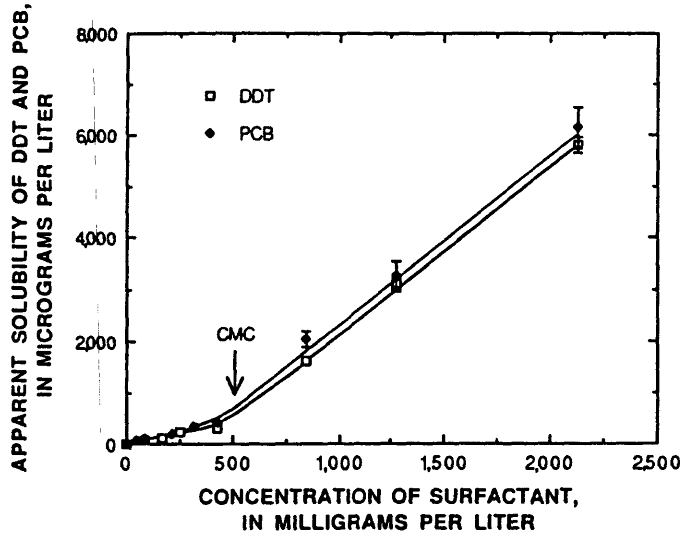

Figure 5. Apparent solubility of DDT and PCB in aqueous solution of LAS.

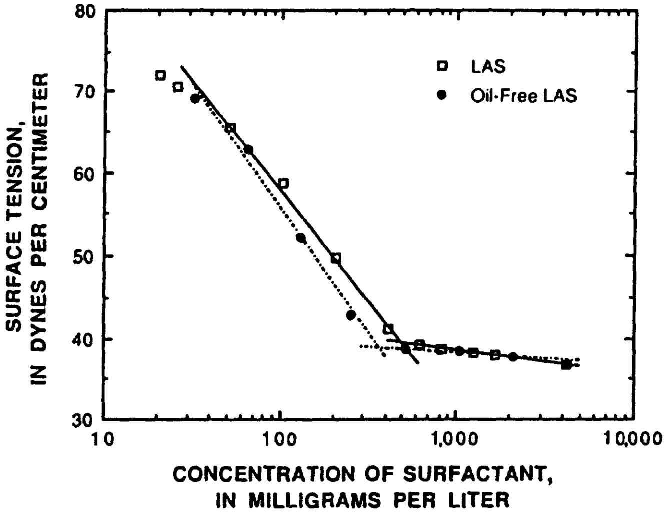

Figure 4. Plot of the surface tension as a function of the logarithm of surfactant concentration for LAS and oil-free LAS.

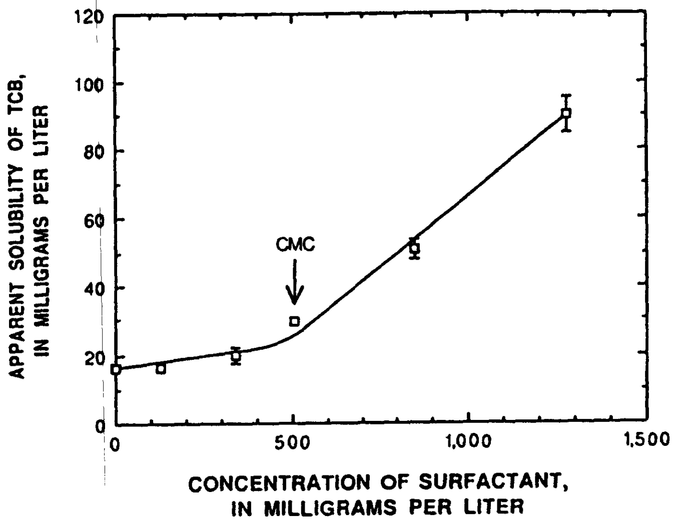

Figure 6. Apparent solubility of 1,2,3-trichlorobenzene in aqueous solution of LAS.

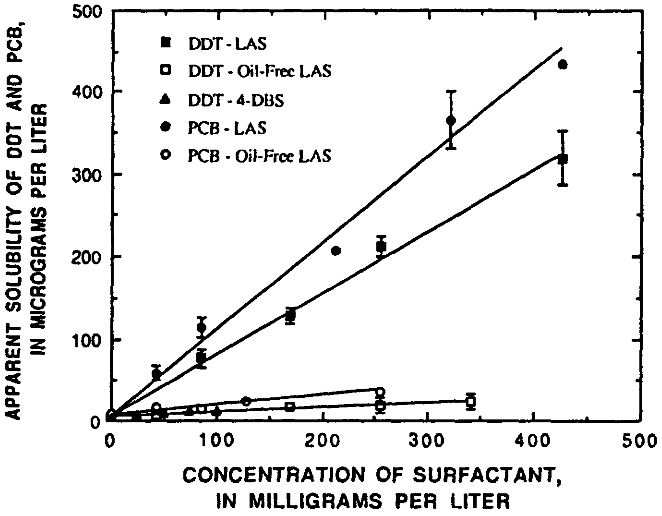

Figure 7. Apparent DDT and 2,4,5,2′,5′-PCB solubilities in dilute aqueous solutions of LAS, oil-free LAS, and 4-DBS.

The comparable solubility enhancement of DDT in oil-free LAS and 4-DBS at low concentration confirms that it is the neutral oil and not the heterogeneity of the LAS that accounts for the unusually high enhancement for LAS below the CMC. Above the CMC the small amount of free oil would be not be expected to have a major effect on solvency in comparison to the micelle; this is verified by the data shown in table 2.

The neutral oil content extracted from the LAS by the method described is about 1.7 weight-percent. This neutral oil does not exist as a separate entity in solution, but is presumably emulsified by a certain quantity of sulfonated components, analogous to the emulsion formed by oil-alkylaryl sulfonate in petroleum sulfonate surfactants. The combined weight of these components in the emulsified phase provides a bulk solvent-like partition efficiency.

With this consideration, the enhancement below the CMC of LAS can be predicted by equating the apparent solute solubility to the amount of oil-surfactant emulsion below the CMC together with the amount of the sulfonated monomers. Hence,

$$S_w^*/S_w = 1 + X_{mn}K_{mn} + X_{em}K_{em}, \qquad (3)$$

where S_w^*/S_w is the ratio of apparent solute solubility enhancement to pure water solubility, and $X_{mn}K_{mn}$ is the concentration and solute partition coefficient of the monomers, and $X_{em}K_{em}$ the concentration and partition coefficient of the emulsion phase. Above the CMC, an additional term $X_{mc}K_{mc}$ can be added to equation 3 to account for the enhancement contribution by the micelle.

With the above equation, an estimate of the emulsion mass below CMC can be made. Using log K_{mn} = 4.08 for DDT with the oil-free component of LAS, and log K_{em} = 6.14 as an estimate for the emulsion component of LAS (based on Pyronate 40, which has sulfonated hydrocarbons of the same average molecular weight as LAS), the calculated X_{em} is about 9 to 10 percent of the LAS concentration below the CMC. With a neutral oil content of 1.7 percent, the estimated ratio of oil to surfactant in the emulsion in LAS is in reasonable agreement with the composition of the stable emulsion of Pyronate 40, which contains one part oil and four parts sulfonated hydrocarbons.

The solubility enhancement effect of LAS can be explained by considering it as a mixture of a conventional surfactant and an oil-surfactant emulsion, such as the petroleum sulfonates. The observed efficiency of the low concentrations of emulsions as found with PSO and LAS surfactants illustrate the potential importance of such systems, formed by mixtures of surface-active agents and neutral oils, on the enhanced mobility of organic pollutants in aquatic environments.

SUMMARY AND CONCLUSIONS

Although conventional surfactant monomers can have a significant impact on the solubility of organic pollutants only for extremely water-insoluble solutes such as DDT, micelles and oil-emulsion systems can be expected to exhibit markedly greater effects. The results of these studies show the importance of surfactant aggregation in controlling solubility enhancement. Petroleum sulfonate surfactant emulsions act like a separate bulk phase at all concentrations, and are therefore considerably more effective at low concentration than are surfactant monomers. This enhanced solute solubilization can be accounted for by partition interaction of the solute, with the emulsion phase providing an effective microscopic nonpolar environment for such interactions. Results of linear alkylbenzenesulfonate point out that even very low amounts of emulsion within a multicomponent surfactant can lead to substantial enhancement of organic compounds. This information gives a basis for predicting the effect of an emulsified phase formed in natural water on the mobility of contaminants.

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ANALYSIS OF ATRAZINE METABOLITES BY ENZYME-LINKED IMMUNOSORBENT ASSAY AND GAS CHROMATOGRAPHY/MASS SPECTROMETRY

By E.M. Thurman[1], Michael Meyer[1], *and* C.D. Adams[1]

ABSTRACT

Enzyme-linked immunosorbent assay and gas chromatography/mass spectrometry methods were developed and tested for the principal metabolites of atrazine, which include hydroxyatrazine, deisopropylatrazine, deethylatrazine, and didealkylatrazine. Methods developed included determination of cross reactivity by enzyme-linked immunosorbent assay, an isolation by solid-phase extraction, and analysis by either enzyme-linked immunosorbent assay or gas chromatography/mass spectrometry. The cross reactivity of the metabolites by enzyme-linked immunosorbent assay was slight compared to that of the parent compound atrazine; 50-percent inhibition values were 0.4 micrograms per liter for atrazine, 28 micrograms per liter for hydroxyatrazine, and 30 micrograms per liter for deisopropylatrazine and deethylatrazine. No cross reactivity was found for didealkylatrazine. The loss of alkyl side chains resulted in decreased cross reactivity. The metabolites were isolated from water on a carbon-18 (C_{18}) solid-phase cartridge for gas chromatography/mass spectrometry analysis. Adsorption capacity factors for the metabolites decreased with increasing water solubility; didealkylatrazine had the least capacity. Gas chromatography/mass spectrometry was attempted on each of the metabolites; however, both didealkylatrazine and hydroxyatrazine required derivatization with pentafluoropropionic anhydride before gas chromatography/mass spectrometry analysis.

INTRODUCTION

Agricultural practices may be causing widespread degradation of water quality in the Midwestern United States (Humenik and others, 1987). Approximately three-fourths of all preemergent herbicides used in the United States are applied to row crops in this 12-State area. Because herbicides are water soluble and commonly volatile, a potential exists for the leaching of herbicides into ground and surface water (Sun, 1988), as well as aerial transport and occurrence in precipitation (Glotfelty and others, 1984). Regional studies conducted in the United States show widespread detection of herbicides in ground water (Hallberg, 1989) and surface water (Goolsby and others, 1989); however, much less is known about the metabolites of herbicides and their metabolites. Part of the reason that the metabolites have not been studied as extensively as parent compounds is the difficulty in isolating and analyzing them. Thus, we examined enzyme-linked immunosorbent assay (ELISA) and gas chromatography/mass spectrometry (GC/MS) as methods for analysis of the four major metabolites of the herbicide, atrazine, in water samples.

Objectives of our paper are to report results on (1) the cross reactivity of the four principal metabolites by ELISA, (2) the isolation procedures for the four metabolites by solid-phase extraction, and (3) the derivatization procedure for the nonvolatile metabolites, hydroxyatrazine and didealkylatrazine.

EXPERIMENTAL METHODS

Methanol and ethyl acetate were pesticide-grade solvents. Atrazine was obtained from Supelco[2] (Bellefonte, Pa.); the atrazine metabolites, deethylatrazine, deisopropylatrazine, didealkylatrazine, and hydroxyatrazine were obtained from Ciba Geigy (Greensboro, N.C.). The C_{18} cartridges contained 360 milligrams of 40-μm (micrometer) C_{18}-bonded silica. Deionized water was charcoal filtered and glass distilled prior to use. Standard solutions were prepared in methanol, and phenanthrene-d_{10} was used as an internal GC/MS quantitation standard.

Res-I-Mune kits (ImmunoSystems Inc., Scarborough, Maine) were used for the cross-reactivity studies by immunoassay. The kits use polyclonal antibodies that are coated on the walls of a polystyrene test tube and an enzyme conjugate that was prepared by a covalently binding atrazine to horseradish peroxidase by a modified carbodiimide technique (Bushway and others, 1988). ELISA was used to test for triazines; ELISA is a colorimetric assay that is inversely proportional in color to the concentration of atrazine present.

The C_{18} cartridges were prepared by washing with 3 mL (milliliters) of methanol, 3 mL of ethyl acetate, 3 mL of methanol, and 2 mL of distilled water. The compounds, deethylatrazine, deisopropylatrazine, and didealkylatrazine were isolated on C_{18} and eluted with 2 mL of ethyl acetate. Hydroxyatrazine was eluted with methanol instead of ethyl acetate.

Derivatization consisted of adding 100 μL (microliters) of pentafluoropropionic anhydride (PFPA) to 1 μg (microgram) of each metabolite and sealing the contents in a screw-cap test tube and heating at 75 °C (degrees Celsius) for 15 minutes. The tube was cooled and the contents evaporated to dryness at 50 °C under nitrogen. The sample was taken up in 100 μL of ethyl acetate and injected onto the GC/MS under conditions stated.

GC/MS analyses of the eluates were performed on a Hewlett-Packard Model 5890A gas chromatograph (Palo Alto, Calif.) and a 5970A mass selective detector (MSD). Operating conditions were as follows: ionization voltage, 70 electron volts; ion-source temperature of 250 °C; electron multiplier, 300 volts above autotune; direct capillary interface at 280 °C tuned daily with perfluorotributylamine; and 50 milliseconds dwell per ion. A fused-silica capillary column of methylsilicone with a film thickness of 0.33 μm, 12 meter x 0.2 millimeter I.D., separated the herbicides with helium as a carrier at 1 mL per minute and a head pressure of 35 kilopascals (Thurman and others, 1990). Scans were done from 50 to 800 atomic mass units.

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[1] U.S. Geological Survey, Lawrence, Kans.

[2] The use of brand, firm, or trade names in this paper is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

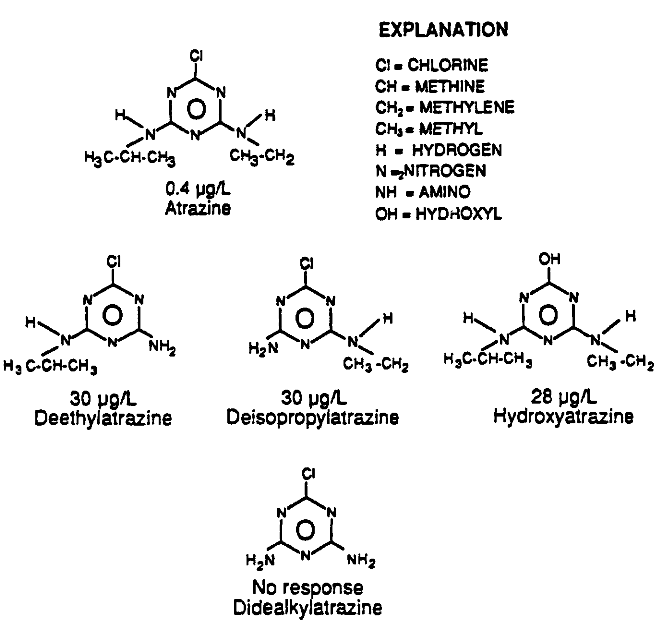

Figure 1. Chemical structure and cross reactivity for atrazine and its metabolites with enzyme-linked immunosorbent assay (ELISA) (expressed as the concentration required for 50-percent inhibition, in units of micrograms per liter as IC_{50}, which is the concentration for 50-percent inhibition of the enzyme).

RESULTS AND DISCUSSION

ELISA and Solid-Phase Extraction

The cross reactivity of the metabolites and their structure are as shown in figure 1. Atrazine has a cross reactivity that is most sensitive with a 50-percent inhibition concentration (IC_{50}) of 0.4 µg/L micrograms per liter. The IC_{50} for hydroxyatrazine was 28 µg/L, for deethylatrazine and deisopropylatrazine it was 30 µg/L, and for didealkylatrazine there was no response. The cross reactivity appears to be related to the alkyl side chain of the molecule (Thurman and others, 1990). Because the dealkylated metabolites remove either one side or the other of the side chain, cross reactivity is dramatically reduced. Thurman and others (1990) concluded that this was the case for the entire family of triazine herbicides, and that the greatest cross reactivity was associated with the structure that most closely resembles atrazine. Hydroxyatrazine, on the other hand, has a structure quite similar to that of atrazine but with low reactivity, presumably because of the enol-keto form of hydroxyatrazine or perhaps because of structural relations caused by hydrogen bonding of water to the phenolic hydroxyl group of the compound.

The volume of water required for the breakthrough of the parent compound atrazine (3,200 mL) and three of its metabolites, deethylatrazine (400 mL), deisopropylatrazine (225 mL), and didealkylatrazine (25 mL), decreased as a function of water solubility. Hydroxyatrazine was not tested in breakthrough experiments. Didealkylatrazine had the least capacity for the resin and was the most water soluble of the metabolites. Its resin capacity was followed by that of deisopropylatrazine, which is next in water solubility, and then by that of deethylatrazine and the parent compound atrazine. The increase in capacity was exponential; an increasing number of carbon atoms was present on the degradation product. Thus, we were unable to improve recovery efficiencies for didealkylatrazine with this isolation procedure. Hydroxyatrazine was recovered efficiently from a 100-mL sample, which was based on the result of placing a second cartridge behind the first cartridge.

Elution efficiencies also were determined for all the compounds, and it was found that didealkylatrazine, deethylatrazine, and deisopropylatrazine eluted effectively with ethyl acetate, but hydroxyatrazine did not. Methanol was tested as an elution solvent and worked well for all three compounds. Unfortunately, the difficulty with using methanol as an elution solvent is that many polar compounds, such as humic material and colored organic acids, are also eluted with this solvent.

GC/MS Analysis

The following abbreviations, each representing a chemical structural group (fig. 1), describe the derivatized triazine compounds analyzed by GC/MS (Cook, 1987):

C--chlorine
I--isopropyl group
E--ethyl group
A--amino group
T--triazine
O--oxygen
P--pentafluropropionic anhydride group.

For example, CIET describes the chemical structure of atrazine; CIAT, deethylatrazine; CEAT, deisopropylatrazine; CAAT, 2-Chloro-4, 6-diamino-s-triazine; and OIET, hydroxyatrazine. Whenever the derivatization includes the addition of a pentafluoropropionic anhydride (PFPA) group, a "P" is used in the structure abbreviation. For example, C(IP)PT describes the structure of deethylatrazine derivatized at the primary amino group and at the secondary amino group containing the isopropyl group.

Figure 2 shows the chromatogram for a derivatization of a mixture of CIET, CIAT, CEAT, CAAT, and OIET that was injected onto the GC/MS 2 hours and 6 hours after derivatization. This chromatogram and its spectra are discussed below by compound.

Atrazine (CIET)

Derivatization of atrazine by the PFPA procedure resulted in three primary peaks (fig. 2, peaks 3, 9, and 10) at 16.76, 18.55, and 19.13 minutes and corresponded to the derivatization of the secondary nitrogens on the atrazine molecule with either or both derivatized. The mono-substituted peaks occurred most commonly with a slight amount of the disubstituted compound. The peaks were stable; less than a 5-percent change in integrated peak area occurred over a 6-hour period.

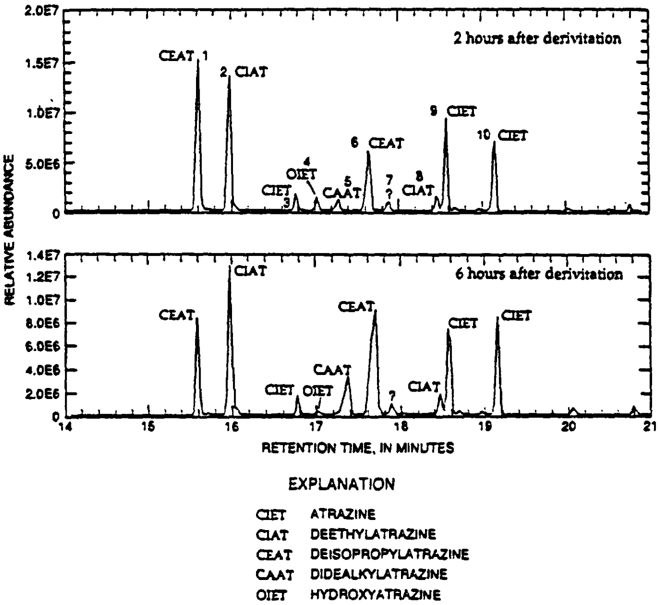

Figure 2. Chromatogram of the derivatized s-triazine mixture (5 micrograms each) with pentafluoropropionic anhydride 2 and 6 hours after derivatization by gas chromatography/mass spectrometry in scan mode.

Deethylatrazine (CIAT)

Derivatization of deethylatrazine by the PFPA procedure produced one primary peak and two secondary peaks (fig. 2, peaks 2, 8, and cochromatographed with peak 6, CEAT). The primary peak was the disubstituted C(IP)PT; the PFPA derivatized at the primary amino group and the secondary amino group. Lesser amounts of the second peaks were produced by derivatization of the amino group only (CIPT) and derivatization at the secondary hydrogen only (C(IP)AT). The primary peak was stable over the 6-hour period although slight conversion of C(IP)PT to CIPT may have occurred over time.

Deisopropylatrazine (CEAT)

Derivatization of deisopropylatrazine by the PFPA procedure resulted in two primary peaks (fig. 2, peaks 1 and 6). Initially, the primary derivative was the disubstituted C(EP) PT at 15.55 minutes, but, over time, substantial conversion of C(EP)PT to CEPT occurred through loss of PFPA by acid hydrolysis on the ethylamino group. The results of this degradation study (fig. 2) indicate that these two derivatives have similar responses by mass spectrometry. Although 55 percent of the C(EP)PT derivative degraded in 4 hours, the CEPT derivative increased by 97 percent over the same period. If the two integrated peaks areas are summed, the combined peak area degraded less than 2 percent in 4 hours.

Didealkylatrazine (CAAT)

Derivatization of didealkylatrazine by PFPA resulted in one primary peak, CPAT, a mono-substituted derivative (fig. 2, peak 5). A peculiar characteristic of this derivative that was not fully understood was that, upon initial analysis by GC/MS, the CPAT derivative is virtually not detected. Upon reanalysis at 6 hours, the peak increased substantially and eventually stabilized, suggesting that there is residual PFPA in the vial that reacts with the compound in the vial.

Hydroxyatrazine (OIET)

Derivatization of hydroxyatrazine by the PFPA procedure results in one primary peak and two secondary peaks (fig. 2, peak 4, others not shown). The major hydroxyatrazine derivative was (OP)I(EP)T, which had a retention time of 17.01 minutes. The other two derivatives were significantly less abundant or not detectable except at high concentrations of hydroxyatrazine.

A significant problem existed with the primary hydroxyatrazine derivative. It was unstable and always degraded rapidly over time. The hydrolysis appeared to occur at the oxygen atom in the molecule with loss of PFPA and loss of volatility. Although a number of attempts were made to stabilize the derivative, including acidification of derivatization solution, not evaporating the derivatives, and cooling samples at 0 °C, none of the procedures helped correct the problem.

CONCLUSIONS

Immunoassay showed a slight cross reactivity for the metabolites relative to the parent compound, atrazine. However, immunoassay could be used on each of the metabolites following some type of preconcentration and separation, such as solid-phase extraction or liquid chromatography. Solid-phase extraction works well for all of the metabolites except didealkylatrazine, which has low affinity for the C_{18} resin. GC/MS was an effective, direct method for two of the metabolites, deethylatrazine and deisopropylatrazine, but derivatization was required for didealkylatrazine and hydroxyatrazine. The derivatization procedure often was sporadic, and results were not reproducible because of acid-catalyzed hydrolysis of the PFPA derivatives. Additional work is needed on other derivatization reagents for the suite of triazine metabolites, including trimethylsilyl derivatives and methylating reagents.

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COMPARISON OF MICROTITRE-PLATE, ENZYME-LINKED IMMUNOSORBENT ASSAY (ELISA) AND GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS) FOR ANALYSIS OF HERBICIDES IN STORM RUNOFF SAMPLES

By M.L. Pomes[1], E.M. Thurman[1], *and* D.A. Goolsby[2]

ABSTRACT

Enzyme-linked immunosorbent assay for triazine and chloro- acetanilide herbicides was used as an inexpensive screening tool for storm runoff at nine stream sites in the Midwestern United States. Microtitre-plate enzyme-linked immunosorbent assay was chosen to provide semiquantitative analysis of herbicide concentrations in storm runoff and to select sample subsets for analysis by gas chromatography/mass spectrometry. In comparing microtitre-plate enzyme-linked immunosorbent assay concentrations to gas chromatography/mass spectrometry concentrations, enzyme-linked immunosorbent assay was found to be an effective measure of triazine herbicides in storm runoff samples. However, for chloro- acetanilides (alachlor and metolachlor), enzyme-linked immunosorbent assay showed a number of false positives and cross reactivity with a metabolite that was not detected by chromatography/mass spectrometry. The correlation coefficients between the triazine enzyme-linked immunosorbent assay and gas chromatography/mass spectrometry results were about 0.9 for atrazine and 0.8 for sum of triazines for the range of 0 to 3 micrograms per liter. Thus, the microtitre-plate enzyme-linked immunosorbent assay provides a good relative measure of storm runoff concentrations of triazine herbicides for that concentration range. Samples with concentrations greater than 3 micrograms/per liter require dilution. Additional work is needed to evaluate the effectiveness of the enzyme-linked immunosorbent assay as a semiquantitative measure of chloro- acetanilide herbicide concentrations in storm runoff samples.

INTRODUCTION

The ability to analyze large numbers of samples for triazine and chloro- acetanilide herbicides inexpensively led to the selection of microtitre-plate, enzyme-linked immunosorbent assay (ELISA) for analysis of storm runoff samples. Microtitre-plate ELISA samples are approximately one-fifth of the cost associated with analyzing comparable samples on the gas chromatograph/mass spectrometer (GC/MS). Storm runoff at nine stream sites in five Midwestern States was sampled to intensively monitor the temporal variation in herbicide concentrations during April-August 1990 (Brown and others, 1990). Stage-activated samplers collected herbicide samples during base flow and storm runnoff. Because an average of 200 samples were collected at each site (Michael Meyer, U.S. Geological Survey, oral commun., 1990), the impracticality of analyzing a total of 1,800 samples by GC/MS and the necessity for a screen to select samples for GC/MS analysis became apparent.

This paper examines the utility of microtitre-plate ELISA as a semiquantitative screen for GC/MS analysis of triazine and chloro- acetanilide herbicides and compares linear regressions of ELISA- and GC/MS-determined concentrations of triazine and chloro- acetanilide herbicides.

METHODS

ELISA Procedure

Res-I-Quant[3] kits consisting of microtitre plates and reagents were used to analyze triazine and chloro- acetanilide herbicides concentrations in storm runoff samples. Each of the 96 wells on the polystyrene microtitre-plate is coated with polyclonal antibodies that adsorb triazine or chloro- acetanilide herbicide molecules depending on the analysis. Res-I-Quant kits additionally used an enzyme conjugate prepared by covalently binding atrazine or alachlor molecules to horseradish perioxidase (Bushway and others, 1988).

Before beginning the ELISA procedure, it was necessary to assign standards and samples to individual wells on the microtitre plate. This was done using the template setup option of the software available with the plate reader. Row A on the microtitre plate was reserved for four standards (deionized water blank; 0.1 µg/L (microgram per liter); 0.5 µg/L; and either 2.0 µg/L for atrazine, or 5.0 µg/L for alachlor) in triplicate. Duplicate samples fill the remaining wells in rows B through H. In addition to the template setup, a file containing instrument settings for the plate reader was created. Such files were called protocol files and contained information regarding the wavelength at which optical absorbances were measured and the calculation of a working curve based on the absorbances and concentrations of the deionized water blank and three standards in Row A.

Eighty µL (microliters) of laboratory standards (triplicate in row A) and samples (duplicate in rows B through G) were added to the plate using 3 adjacent and 2 adjacent channels, respectively, of a 12-channel pipettor. Immediately following the addition of standards and samples, 80 µL of enzyme conjugate were added to each well using all 12 channels of the pipettor. (The enzyme conjugate competes with herbicide molecules for empty antibody-binding sites in the wells of the microtitre plate.) Then the plate was covered with parafilm and allowed to incubate for 1 hour at room temperature while being rotated

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[3] The use of brand, firm, or trade names in this paper is for identification purposes only and does constitute endorsement by the U.S. Geological Survey.

180 rpm (revolutions per minute) on an orbital shaker. Upon completion of the incubation step, the plate was flushed completely and rinsed five times with deionized water, then dried with compressed air. After that, 160 µL of a mixture of substrate and chromogen (mixed in that order) were pipetted into each well using all 12 channels of the pipettor. Again, the plate was covered with parafilm and allowed to incubate for 30 minutes at room temperature while rotating on an orbital shaker at 180 rpm. During the course of this step, the action of the substrate and chromogen on the enzyme conjugate produced a blue color, which was inversely proportional to the analete concentration. This reaction was halted with the addition of 40 µL of sulfuric acid (2.5 normal) solution, which caused the color of the substrate- chromogen mixture to change to yellow. Next, the appropriate protocol was recalled for that microtitre plate, and the plate reader determined the optical absorbances in all of the wells. Output from the plate reader included the standard curve and concentrations for all samples.

Sample Selection for ELISA

Herbicide samples for the storm-runoff study were collected with ISCO and Manning automated samplers. Bottles were unloaded from the samplers in sequence and given sequence numbers that correspond to the time interval between samplings. All of the storm-runoff samples were analyzed for triazine and chloro- acetanilide by ELISA. Inspection of the sample sequence numbers and associated ELISA results gave an indication of the temporal variation in triazine and chloro- acetanilide concentrations. Samples to be analyzed by GC/MS were chosen to delineate high and low parts of the curve showing the change in concentration over time (Michael Meyer, U.S. Geological Survey, oral commun., 1990). Procedures used to extract herbicides from water samples and the GC/MS analyses of herbicides are described by Thurman and others (1990).

ELISA Evaluation

After completion of the GC/MS analyses, results were compared to the concentrations obtained by ELISA. The comparison involved two tasks. First, the distribution of positives and negative detections by ELISA and GC/MS was tabulated to obtain information about the occurrence of false positives and negatives produced by both the triazine and chloro- acetanilide herbicides Res-I-Quant kits. False positives are the herbicide detections made using the ELISA technique that are not confirmed by GC/MS, whereas, false negatives are herbicide detections made by GC/MS that are not confirmed by ELISA. Second, ELISA concentrations were plotted as a function of GC/MS concentrations. The plots included ELISA triazine concentration compared to GC/MS results for atrazine and sum of all triazines determined using the method outlined in Thurman and others (1990); along with ELISA chloro- acetanilide concentrations contrasted to GC/MS results of alachlor, metolachlor, and sum of chloro- acetanilides (arithmetic sum of alachlor plus metolachlor) concentrations. Linear regressions and correlation coefficients were calculated for each plot.

DISCUSSION

The results of the tabulation of positives and negatives for triazine and chloro- acetanilides by ELISA and GC/MS are illustrated in figure 1. Of a total of 88 samples, triazine microtitre-plate ELISA had the largest number of GC/MS confirmations of positives (85), no false positives, and 3 false negatives by GC/MS. The false negatives originated from the difference in reporting limits for the two methods. The reporting limit for the triazine microtitre-plate ELISA traizine was 0.1 µg/L (micrograms per liter), whereas the reporting limit for GC/MS analyses was 0.05 µg/L. The false negatives that were encountered entailed concentrations, determined by GC/MS, that exceeded the 0.1-µg/L reporting limit.

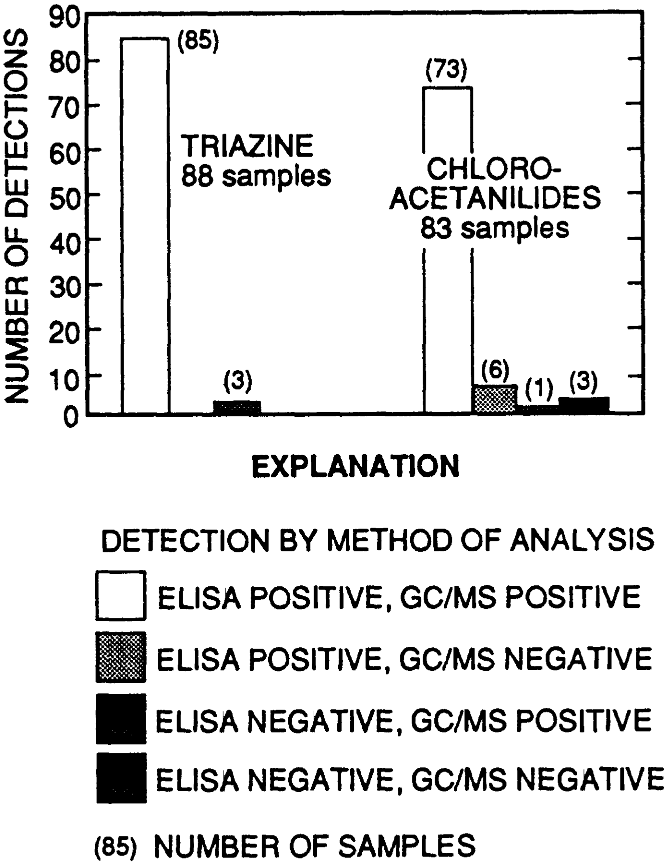

Figure 1. Tabulation of the distribution of positive and negative detections by enzyme-linked immunosorbent assay (ELISA) and gas chromatography/mass spectrometry (GC/MS) analysis of triazine and chloro- acetanilide herbicides.

The chloro- acetanilide microtitre-plate ELISA presented a different distribution of confirmed detections of positives and negatives (fig. 1). Of 83 samples, six "outright" false positives were detected. These false positives were not confirmed by GC/MS. The "outright" false positives show that a compound, perhaps a metabolite of alachlor, has cross reactivity for the alachlor ELISA but is not detectable on the GC/MS. Feng and others (1990) noted a similar problem with their alachlor ELISA and found that some alachlor

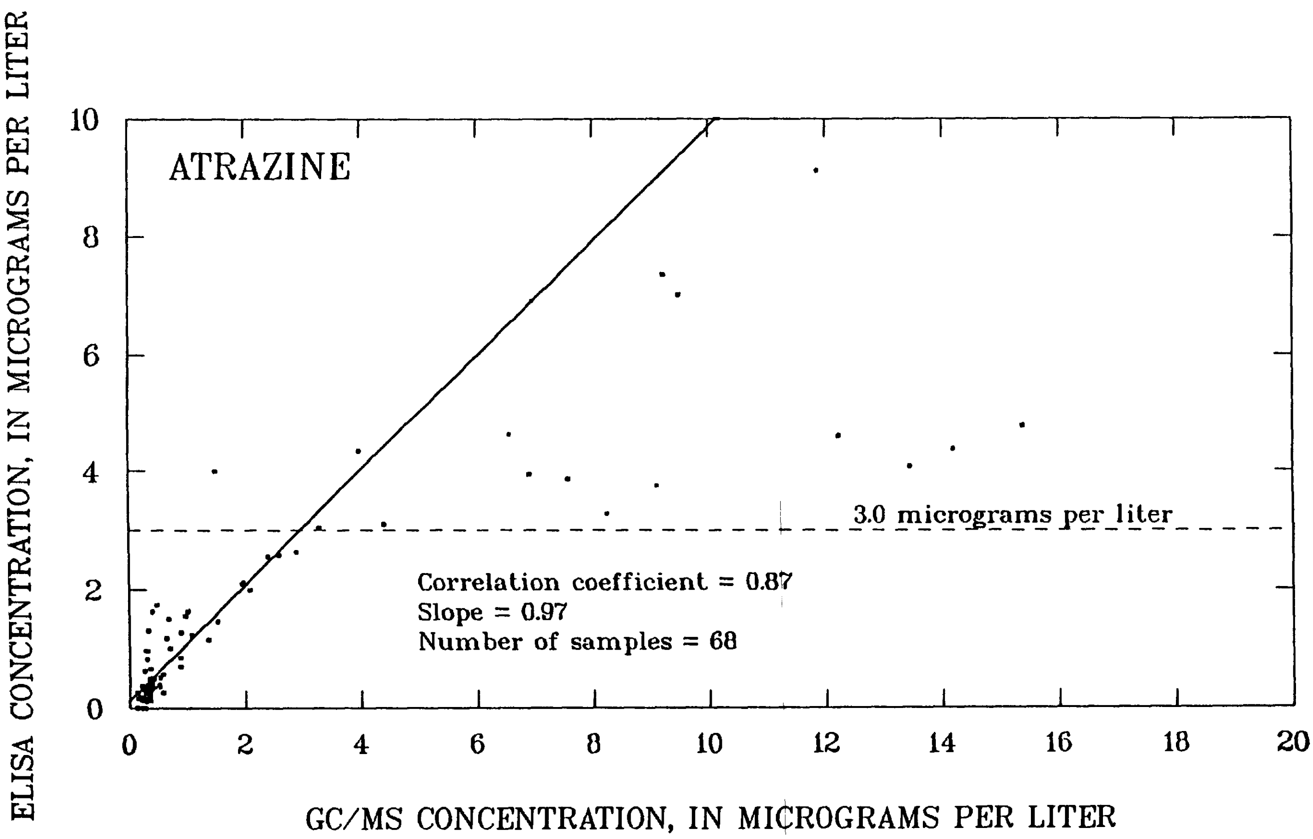

Figure 2. Atrazine concentrations determined by enzyme-linked immunosorbent assay (ELISA) as a function of concentrations determined by gas chromatography/mass spectrometry (GC/MS). The dashed line through 3.0 micrograms per liter on the ELISA concentrations axis is the limit below which the linear regression was calculated. Data above this value required extrapolation beyond the 2.0 microgram per liter atrazine high standard.

metabolites had significant cross reactivity. In addition, the occurrence of positives marked by the trace presence of metolachlor also demonstrates cross reactivity with that compound; seven choro- acetanilide microtitre-plate ELISA positives were confirmed by the GC/MS detection of metolachlor concentrations greater than the 0.05 μg/L reporting limit for that method.

Inspection of the plot of triazine microtitre-plate ELISA concentrations contrasted to GC/MS-determined concentrations of atrazine reveals two trends (fig. 2). First, a relatively straight line is apparent on the plot up to about 3 μg/L for ELISA-determined concentrations. Second, above 3 μg/L, agreement of triazine microtitre-plate ELISA concentrations and GC/MS-determined concentrations of atrazine is poor. ELISA concentrations were calculated as a standard curve, with 2 μg/L as the high standard for atrazine. Concentrations greater than 3 μg/L required extrapolation.

The scatter of points between 3 and 16 μg/L for GC/MS atrazine concentrations also represents saturation of the atrazine ELISA. Saturation occurs because each well contains a finite number of polyclonal antibodies bound to the inside of a well; samples containing larger concentrations overwhelm the antibodies because only so much atrazine can bind with the antibodies. The limit of saturation for atrazine using a 2-μg/L high standard then appears to be between 3 and 5 μg/L even though greater concentrations were determined by the GC/MS. Because of the saturation of the atrazine ELISA and extrapolation beyond the 2-μg/L high standard, the technique can only indicate positive detections of atrazine, unless samples are diluted.

For triazine concentrations less than 3 μg/L, the plot has a slope of 0.97 and a correlation coefficient of 0.87. Thus, microtitre-plate ELISA appears to be a good measure of atrazine concentrations in storm-runoff for concentrations less than 3.0 μg/L.

The plot of microtitre-plate ELISA triazine concentrations as a function of GC/MS concentrations for sum of all triazine concentrations shows more scatter of data points (fig. 3). Sum of all triazine concentrations is simply the arithmetic sum of triazine herbicides identified using the method outlined by Thurman and others (1990). For concentrations less than 3 μg/L, the plot has a slope of 0.28 and a correlation coefficient of 0.77. Having a slope less than 1.0 indicates that the response to ELISA is less than the summed GC/MS response for the sum of triazine concentrations. More work needs to be done to quantify the cross reactivity of other triazine herbicides with the atrazine microtitre-plate ELISA.

Linear regressions for plots of ELISA alachlor concentrations as a function of GC/MS concentrations for alachlor, metolachlor, and sum of acetanilides did not produce any significant statistical relations. Thus, the

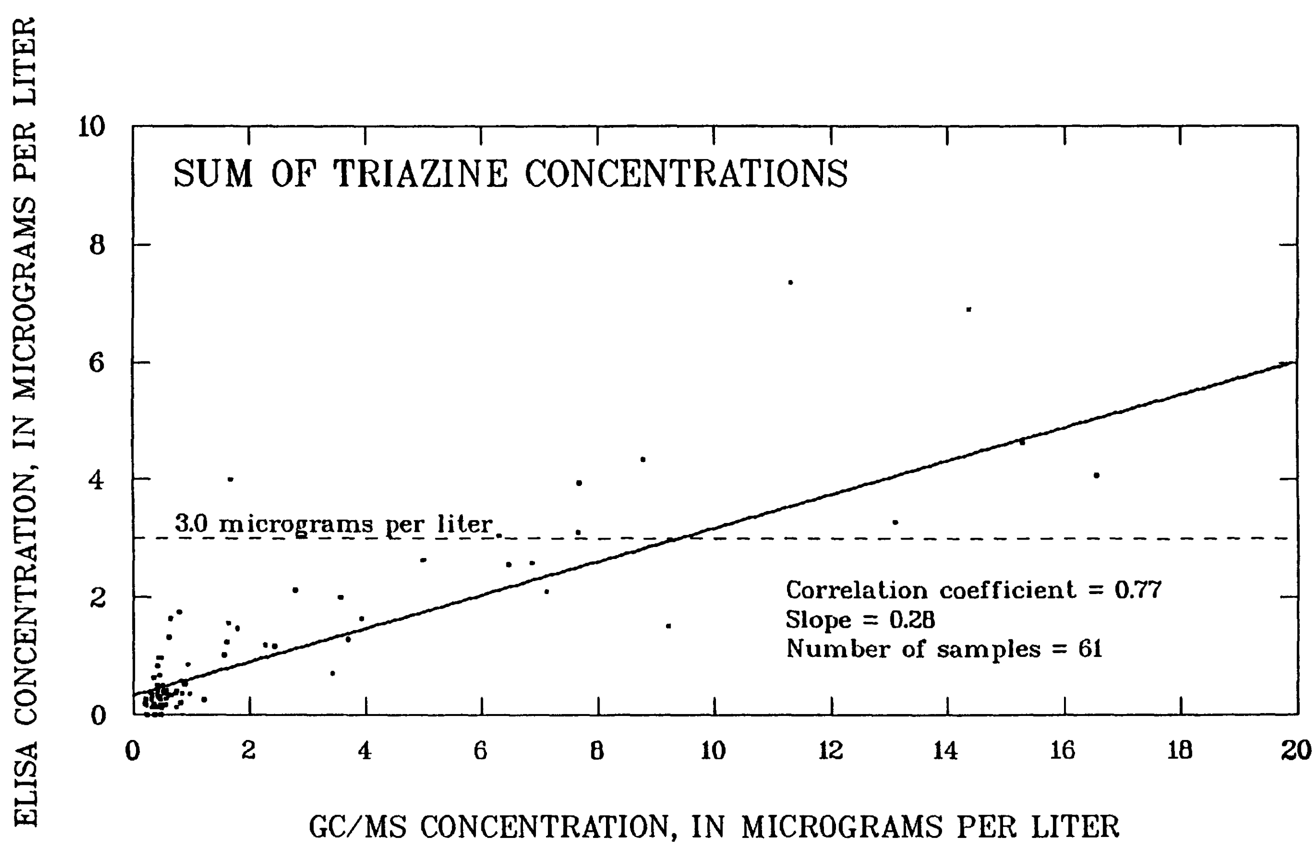

Figure 3. Sum of triazine concentrations determined by enzyme-linked immunosorbent assay (ELISA) as a function of concentrations determined by gas chromatography/mass spectrometry (GC/MS).

alachlor ELISA appears to be a reliable indication of the presence of alachlor in storm-runoff but not a semiquantitative measure. More work needs to be done to refine the alachlor ELISA technique so that a semiquantitative relation of ELISA-determinted alachlor concentrations to GC/MS-determined alachlor concentrations can be found.

CONCLUSIONS

For a sample size of 88 samples, the triazine microtitre-plate ELISA produced no false positives. The false negatives that were detected by GC/MS entailed atrazine concentrations less than the 0.1-µg/L reporting limit for triazine microtitre-plate ELISA.

For a sample size of 83 samples, the choroacetanilide microtitre-plate ELISA produced 6 false positives compared to GC/MS results. A metabolite of alachlor or metolachlor not detectable with the GC/MS may cause the false positives. Also, the chloro- acetanilide microtitre ELISA showed cross reactivity with metolachlor because of positives detections confirmed by the GC/MS detection of metolachlor without any alachlor.

Microtitre-plate ELISA is a good measure of atrazine and triazine concentrations in storm runoff for concentrations less than 3 µg/L. At greater concentrations, triazine microtitre-plate ELISA only indicates the presence of triazine herbicides; a semiquantitative measure will exist only when these samples are diluted. Likewise, the chloro-acetanilide microtitre-plate ELISA only indicates the presence of chloro- acetanilide herbicides and has not been demonstrated to be a semiquantitative measurement.

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DESCRIPTION OF WATER-QUALITY SYNOPTIC EXPERIMENTS IN THE COLORADO RIVER

By H.E. Taylor[1] *and* R.C. Averett[1]

ABSTRACT

Synoptic experiments provide a way of assessing the water quality of complex large river systems. An example is presented of the use of the synoptic approach for assessing water quality along 470 kilometers of the Colorado River (Lake Powell through the Grand Canyon to Columbine Falls). The results of the synoptic study will be used to design future research studies and experiments on the various hydrologic processes impacting the Colorado River ecosystem.

INTRODUCTION

Synoptic experiments are used to assess, in a comprehensive manner, the characteristics or conditions of a system at a fixed point in time. Sampling is coordinated and carried out simultaneously at several carefully predetermined locations. These sites are selected to provide the maximum amount of information regarding important inputs or disturbances to the system.

The purpose of this type of experiment is to permit the development of a general understanding of the system and to provide a large data base of information for use in defining the spatial characteristics in as much detail as possible. In addition, the data base is useful for establishing protocols and direction for much more detailed and specific future investigations and research studies.

In the case of large river systems, repetitous sampling, closely spaced in time, can provide additional information regarding short-term variations in chemical and biological water quality in relation to a variety of physical parameters, including hydrologic, meteorlogic, and diel conditions. Executing water-quality synoptic experiments during different seasons of the year can also provide information concerning long-term temporal variations. Collectively, this information can provide a rapid and comprehensive analysis of the status and variability of the water quality in a large and complex river system. Differentiation of unstable properties, the significance of the magnitude and diversity of important components, and the sensitivity of their response to physical variables provide a systematic way to evaluate present and future water-quality conditions. This paper describes a large water-quality synoptic experiment conducted on the Colorado River.

CASE STUDY

As a large-river example, a water-quality synoptic experiment was conducted on the Colorado River, November 5 and 6, 1990. Ten mainstream river stations and six tributary stations (at confluence) were selected for water-quality measurements and sample collection for chemical and biological analysis (see fig. 1). A total of 470 river kilometers (the tailwater of Glen Canyon Dam to Columbine Falls) was included in the synoptic experiment. Included also was the forebay of Lake Powell formed by Glen Canyon Dam where the water that would ultimately be released into the river was sampled. The Colorado River example is the basis for a major environmental impact assessment on the Lake Powell-Glen Canyon Dam-Colorado River ecosystem.

Sixty-eight people (all but four from the U.S. Geological Survey) (USGS), participated in the synoptic experiment. At each mainstream sampling station, or combination mainstream-tributary station, a team leader was designated. The team leader was assigned the responsibility for directing the sampling, processing samples, and recording field data. Training of team leaders and team members on field measurements and sample collection was performed on October 29, 1990, at Lees Ferry, Ariz. Three training sessions, including 3 to 4 hours of classroom instruction and riverside equipment demonstration and use, were presented by scientists from the USGS National Research Program.

After training and equipment testing, personnel were transported to their assigned sampling locations. Personnel were at their stations by late Saturday, November 3, 1990. Sunday, November 4, 1990, was used to establish local sampling schemes, and field-measurement sites, and to practice measurements and sample collection.

Of the 10 mainstream Colorado River sampling stations, 6 have cableways that cross the river for discharge measurement and sample collection. The cableways were used in the synoptic experiments for water-sample collection. At stations where a cableway was not available, sampling and measurements were performed using a winch and boom mounted on a boat. In small tributaries, samples were collected by wading. All samples for chemical analysis were collected by depth-integrated discharge-weighted procedures. The samples from the cableways and by boat were collected by the D-77 sampler, modified to permit use of the collapsible-bag technique as described by Meade and Stevens (1990). Samples collected by wading used the DH-81 sampler. In both cases, sampling equipment was designed and configured to maintain the integrity of samples for low-level trace-element analysis.

Field measurements and sample collection began at 0600 hours on Monday, November 5, 1990, and continued every 6 hours thereafter, until and including midnight, November 6, 1990. This scheme provided eight measuring and sampling times over a 48-hour period, accommodating diel variations and fluctuating river stage caused by variable water release from Glen Canyon Dam. All subsequent water samples for chemical and biological analysis were

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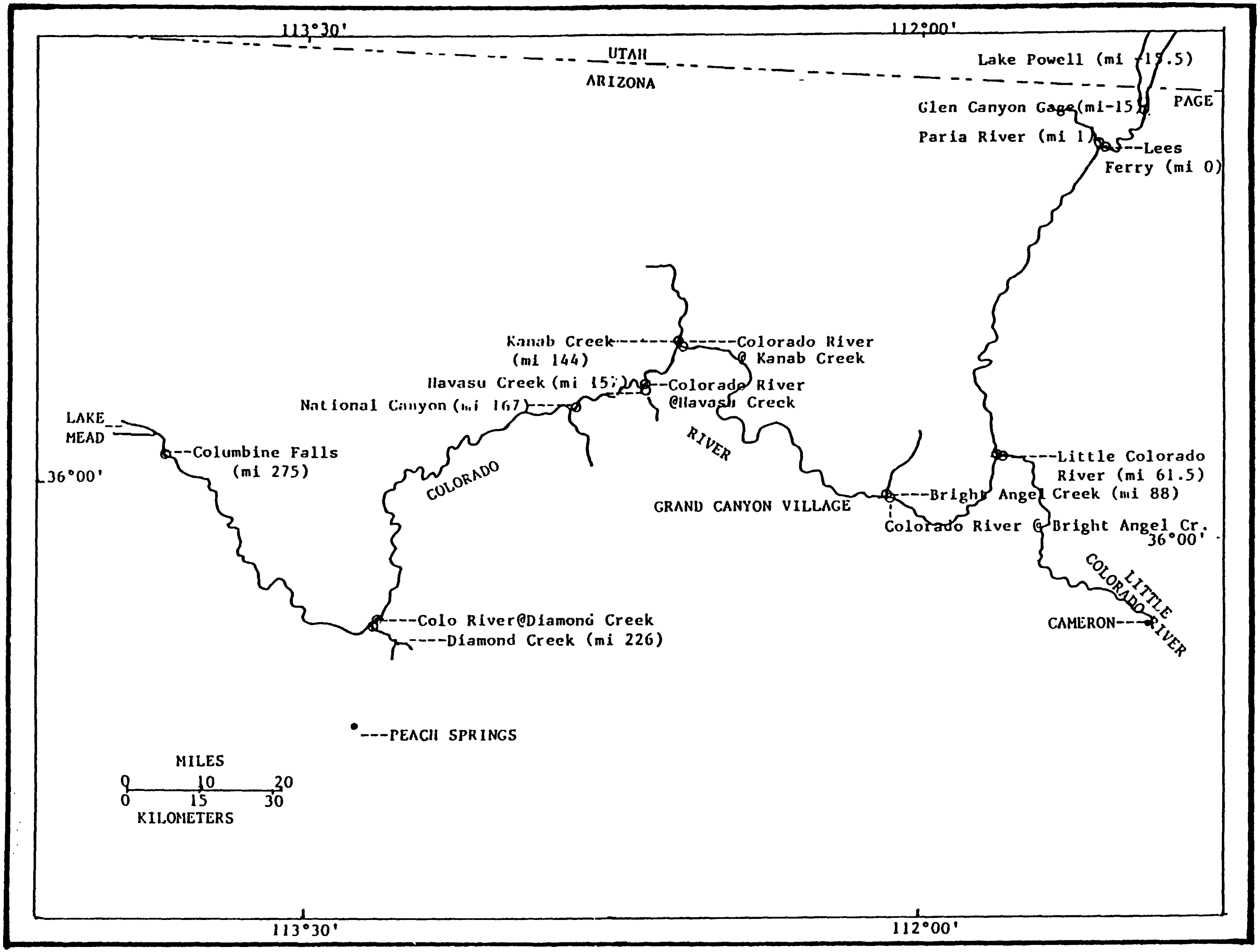
113°30'
UTAH
ARIZONA
112°00'
Lake Powell (mi -15.5)
Glen Canyon Gage (mi-15)
PAGE
Paria River (mi 1)
--Lees Ferry (mi 0)
Kanab Creek (mi 144)
Colorado River @ Kanab Creek
Havasu Creek (mi 157)
Colorado River @Havasu Creek
National Canyon (mi 167)
LAKE MEAD
--Columbine Falls (mi 275)
36°00'
COLORADO
RIVER
GRAND CANYON VILLAGE
----Bright Angel Creek (mi 88)
Colorado River @ Bright Angel Cr.
----Little Colorado River (mi 61.5)
36°00'
LITTLE COLORADO RIVER
CAMERON
----Colo River@Diamond Creek
----Diamond Creek (mi 226)
---PEACH SPRINGS
MILES
0
10
20
0
15
30
KILOMETERS
113°30'
112°00'

Figure 1. Colorado River showing sampling station localities and river miles from Lees Ferry for the November 5-6, 1990 USGS water-quality synoptic studies. (o - indicates sampling localities.)

Table 1. *Chemical determinations made on synoptic samples*

- Nutrients
  - Nitrate
  - Phosphate
  - Ammonium ion
  - Dissolved nitrogen
  - Dissolved phosphorus
  - Dissolved organic carbon
- Major ions
  - Calcium
  - Magnesium
  - Sodium
  - Potassium
  - Silica
  - Chloride
  - Sulfate
- Trace elements
  - Aluminum
  - Arsenic
  - Barium
  - Beryllium
- Trace elements (cont.)
  - Boron
  - Cadmium
  - Chromium
  - Cobalt
  - Copper
  - Iron
  - Lithium
  - Lead
  - Manganese
  - Mercury
  - Molybdenum
  - Nickel
  - Selenium
  - Strontium
  - Thallium
  - Uranium
  - Vanadium
  - Zinc

field-filtered and preserved, if necessary, at the time of collection. The samples were shipped chilled to the USGS National Research Program laboratory at Arvada, Colo., for laboratory analysis (Taylor and others, 1990).

Field measurements at each station included river and tributary discharge, temperature, alkalinity, specific conductance, pH, dissolved oxygen concentration, and Secchi-disk depth. About 780 field measurements were made during the synoptic experiment. Water samples were collected for analysis of chemical and biological characteristics and suspended-sediment concentration. Chemical determinations are listed in table 1. Biological determinations included drift biomass collected with 100-millimeter orifice-diameter nets at all sites and 0.5-meter orifice-diameter nets at selected sites; benthic invertebrates at the lowest flow in the main stem Colorado River and at sampling-time flow in the tributaries; phytoplankton and zooplankton abundance; and, at several stations, chlorophyll *a* concentration (Averett and Iwatsubo, in press). About 2,300 water samples were collected for chemical and biological measurements. In addition to the specific determinations, team leaders and team members were careful to make detailed notes on river conditions, including floating material in the river, and to take pictures of the river and sampling sites at the time of the synoptic experiment.

SUMMARY

Synoptic experiments provide a way of rapidly evaluating water quality in large river systems. These data are especially useful in guiding future research directions. By designing time variation in the synoptic sampling, additional information can be obtained regarding temporal changes in chemical and biological properties.

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THE ROLE OF BED SEDIMENTS AND DRIFT IN THE TRANSPORT AND FATE OF METALLO-ORGANIC COMPOUNDS IN THE CALCASIEU RIVER ESTUARY, LOUISIANA

By Nancy S. Simon[1] *and* Janet F. Morrison[2]

ABSTRACT

This paper reports the progress of an ongoing study of the reactions in riverine and estuarine environments between metals and organic matter with respect to the transport of metals. In this study, supercritical fluids were used to fractionate organic compounds and metallo-organic complexes from bottom sediment and drift from the Calcasieu River Estuary. Bottom sediment, interstitial water, and algal drift samples were collected from sites in a tributary of the Calcasieu River, Louisiana, that receives industrial effluent. The samples were analyzed for heavy metals, including copper, chromium, and lead. Concentrations of metals in interstitial water did not correlate with total metal concentrations in the sediment. Concentrations of heavy metals in the drift were as much as two orders of magnitude larger than in the bottom sediment. When supercritical carbon dioxide and carbon dioxide plus methanol as a modifier were used to fractionate the organic matter in the drift, the amounts of heavy metals that were recovered in the extracts differed among the metals. Infrared and ultraviolet spectroscopy have been used to identify the functional groups with which individual metals are complexed.

INTRODUCTION

The results of a 1986 indepth study of the sediment from four sites in the Calcasieu River indicated that chromium (Cr) associated with sediment organic matter was contributing to the elevated levels of chromium in the interstitial water. The four sites are located in figure 1 and are Buoy-130 (B-130), Bayou d'Inde (BDI), CITGO, and BURTONS. Site B-130 is also identified as site 17 in the 1988 and 1990 studies; it is upstream from Lake Charles and close to a saltwater barrier that prevents marine water from flowing into the upper Calcasieu River. The location is considered unaffected by industrial discharges. The site at BDI is located south of site B-130 at the confluence of the Calcasieu River and Bayou d'Inde. The third site, CITGO, is close to, and downstream from, a loading dock and holding pond of a petroleum refinery. BURTONS, the fourth and most downstream site, is upstream from a boat-repair yard. Data from these four sites indicated that BDI was the site at which manmade contamination had occurred and was occurring to the greatest extent.

Collaborative studies with the U.S. Environmental Protection Agency (USEPA) were done in Bayou d'Inde in 1988 and 1990. These studies compared the results of toxicity tests with the chemistry of the sediment to which selected organisms were exposed over time under controlled conditions. The USEPA conducted the toxicity tests and the U.S. Geological Survey did the sediment chemistry. Even though the tests were inconclusive because the experimental conditions in the laboratory did not match the environmental conditions existing in Bayou d'Inde, the two independent tests conducted 2 years apart showed that the sediment from half to all of the sites from BDI provided conditions resulting in 100-percent mortality of sediment feeders. This observation suggests that there is a cause for concern about the condition of the benthic environment. Chemical data were similar for sediment collected in 1988 and 1990 at the mouth of the industrial outfall canal into Bayou d'Inde. For example, mercury concentrations exceeded 1 ppm (part per million) in sediment collected in both years from this site.

The 1990 study focused on the source and method of transport of high concentrations of metals in Bayou d'Inde and subsequently into the mainstream of the Calcasieu River. The water-column concentrations of the metals of interest were not greater in Bayou d'Inde than they were in the Calcasieu River (C.R. Demas, U.S. Geological Survey, oral commun., 1990). Apparently, the dissolved phase is not the means of metals transport. All of the metals of interest are known to complex with organic matter (Cotton and Wilkinson, 1988) and the source of organic matter that could transport these metals was sought.

One source of organic matter not previously investigated, but which contributes organic material to the industrial outfall canal, is algal drift. This is algal matter, including benthic algae and periphyton, that is released to the water column and is free floating when collected by a drift net.

Algae are rich in chlorophyll. Chlorophyll and the degradation products of chlorophyll (for example, phaeophytin) are potential complexers of metals. The heterocylic nature and oxygen, sulfur, and nitrogenous components in the structure of many of the organic molecules that are part of the structure of algal cells, contribute to the binding capacity of these compounds for heavy metals. The efficiency of the bonding between metals and chlorophyll is used in chromatographic separations in which chlorophyll is used as an active bonder of metals (Lautsch and others, 1951).

If the complexes of organic matter and metals could be fractionated without altering their structure, structural information could be determined to delineate the relation between metals and naturally occurring organic matter. Supercritical fluids are capable of fractionating organic matter at low temperatures. When modifiers are required, they are generally innocuous compounds, such as methanol. Supercritical fluids are produced by applying high pressure (100-500 atm (atmospheres); 1,500 to 7,500 pounds per square inch) to gases and elevating the system to the

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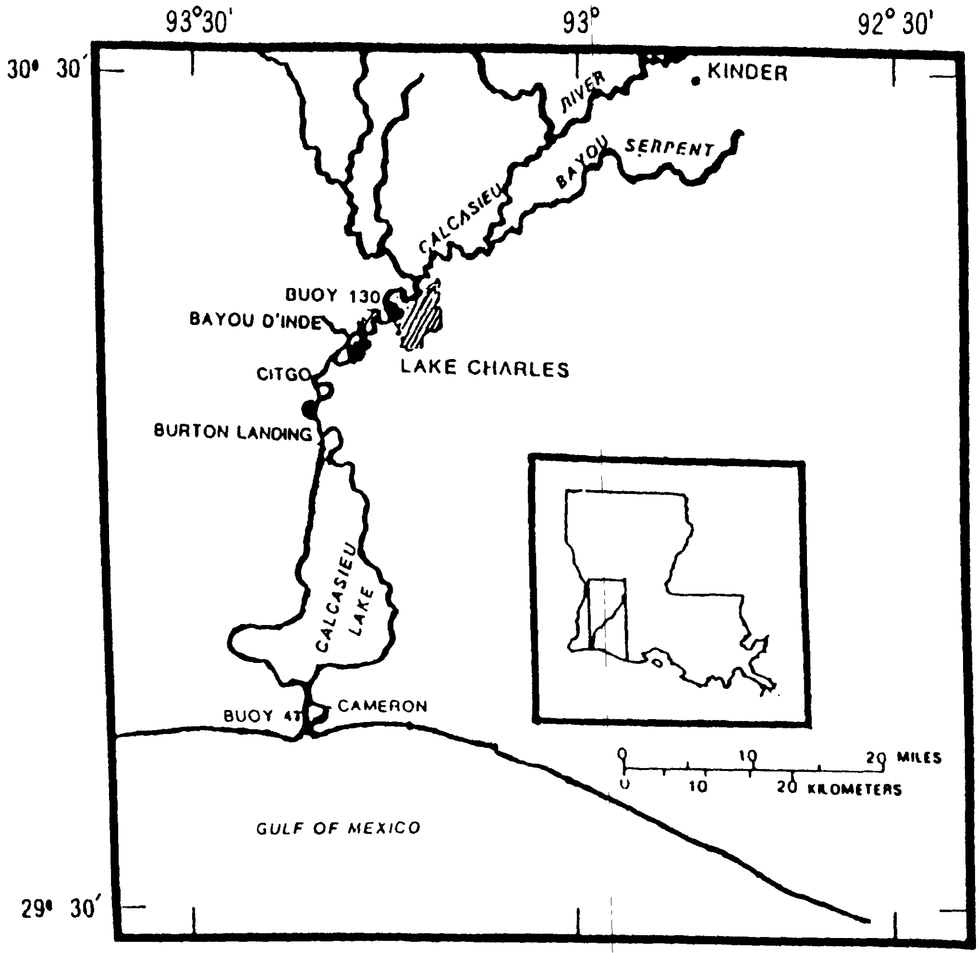

Figure 1. Map of the Calcasieu River and estuary showing sampling sites in May 1986.

temperature at which the liquid becomes a fluid. Varying the pressure and temperature controls the density of the supercritical fluid. Increased pressure and decreased temperature produce more dense, that is, more concentrated supercritical fluids. A phase diagram giving the boundary conditions for a supercritical fluid is shown in figure 2. The working conditions for supercritical fluid carbon dioxide are temperatures above 32 °C (degrees Celsius) and pressures above 73 atm. At these low temperatures, labile compounds such as metallo-organics are stable.

This paper reports the progress of an ongoing study of the reactions between metals and organic matter and the relation between these reactions and the transport of metals in riverine and estuarine environments. The paper will include results of applying supercritical fluids to the fractionation of organic compounds and metallo-organic complexes from bottom sediment and drift from the Calcasieu River Estuary.

METHODS

Bottom-sediment samples were collected using a Teflon[3]-coated stainless steel grab sampler. The sampling locations for the studies in 1988 and 1990 were the same. The sites for the 1990 study are marked in figure 3. Site 4 is 0.18 km (kilometers) downstream from the confluence of Little Bayou d'Inde and Bayou d'Inde. Site 6 is located at the outfall pipe from an oil refinery. Site 3 is at the mouth of the industrial outfall canal. Site 9 is located 0.4 km upstream and site 10 is 0.4 km downstream from the industrial outfall. Site 11 is 0.8 km downstream from the industrial outfall. The site 17 was referred to a site Buoy 130 in the previous studies and is in Lake Charles.

Samples for interstitial water analysis were packed into 40-milliliter centrifuged tubes and covered with screwcaps at the sampling site, returned immediately to the field laboratory, chilled, and centrifuged in a bench-top centrifuge. The centrifuge tubes then were placed in a nitrogen-filled glove bag and the supernatant interstitial-water was filtered through 0.2 µm (micrometer) polycarbonate filters and transferred to vials. The samples for anion analysis were added to the pH 10 eluent used in ion-chromatographic analysis and the neat interstitial water samples for metal analysis were acidified with concentrated nitric acid. Water-column samples were collected with a glass bottle in an epoxy-coated wire basket sampler.

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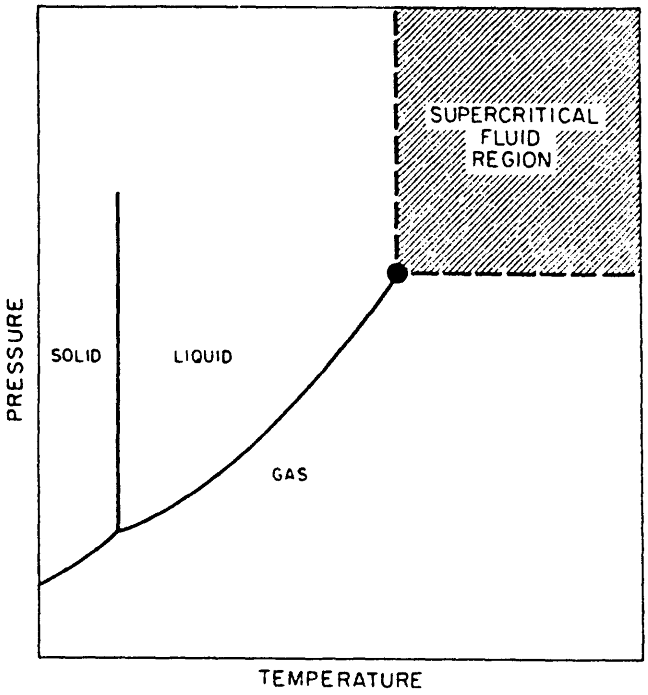

Figure 2. Phase diagram showing conditions for supercritical fluids.

Samples were filtered through 0.2 µm polycarbonate filters. Water column samples were preserved in the same manner as interstitial water samples. Drift samples were collected using a 0.505 millimeters mesh drift net that floated near the surface to the water column at site 3. Material was removed from the net and transferred to glass jars. Samples were refrigerated at the field laboratory. Chemical analyses for total sediment copper (Cu), (Cr) and lead (Pb) were done following the procedures of Horowitz and Elrick (1985). Interstitial water concentrations of Cr, Cu and Pb were determined using the methods described in Simon and others (in press). Total sediment concentrations of ammonium, and interstitial water concentrations of chloride and sulfate, were determined using the methods described in Simon and Kennedy (1987).

Drift samples were air-dried over calcium chloride. Samples were transferred to a cartridge capable of remaining sealed to pressure of at least 400 atm. An Isco 260D syringe pump was used to produce carbon dioxide under pressures of up to 400 atm. When methanol was used as a modifier, it was loaded into an injection loop through which the fluid carbon dioxide entered the cartridge. A column heater was used to hold the extraction column at 45 °C when carbon dioxide was used alone and 65 °C when methanol was added as a modifier. Extractions were done with a 15-minute static step followed by a 30-minute dynamic step. Samples were collected in methanol or hexane in vials at the end of a fused-silica capillary. Flow through the capillary allowed the transfer of the organic compounds dissolved in the supercritical fluid carbon dioxide to the sample-collecting vial at ambient conditions. Samples were evaluated using Fourier Transform Infrared Spectroscopy (FTIR), ultraviolet spectrophotometry, gas chromatography, and atomic absorption spectroscopy. Metal concentrations were determined using atomic absorption spectroscopy methods provided by the manufacturer (Varian, 1982).

RESULTS

The sediment and interstitial-water concentrations of the metals included in this study are listed in table 1. The concentrations are given in ppb (parts per billion). In contrast, preliminary concentrations of Cr, Cu, and Pb in drift samples were 100, 200, and 50 ppm, respectively. Also listed are the interstitial-water concentrations of chloride and sulfate. There was no correlation between the total concentration of metal in the whole sediment sample and the concentration of metal in the associated interstitial water. Cu, Cr, and Pb concentrations tend to be elevated in sediment from sites where the interstitial-water concentrations of chloride are also elevated. Concentrations of Cu in sediments from sites close to the industrial outfall were larger than the concentrations of Cu in sediments

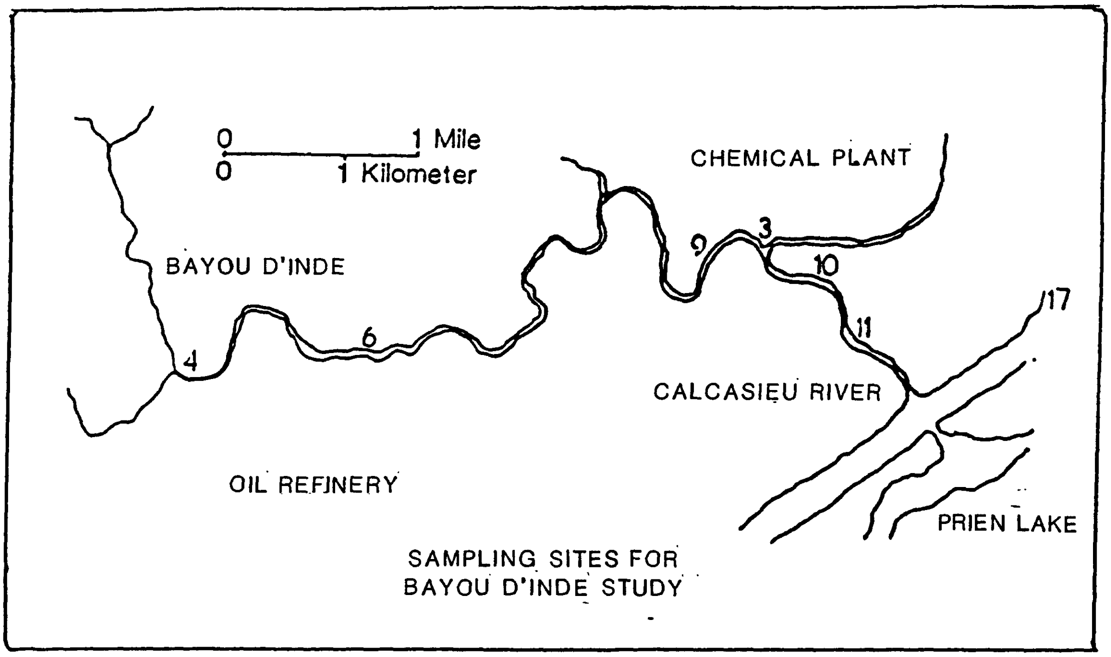

Figure 3. Sketch of Bayou d'Inde showing sampling sites for studies in June 1988 and July 1990.

Table 1. *Total sediment (TS) concentrations of chromium (Cr), copper (Cu), and lead (Pb) in parts per billion (ppb) and interstitial-water (IW) concentrations of Cr, Cu, and Pb in ppb and interstitial-water concentrations of chloride (Cl) and sulfate (SO_4) in millimoles (mmol) per liter for sediments and IW collected from Bayou d'Inde, Louisiana, in July 1990*

Site	TSCr	TSCu	TSPb	IWCr	IWCu	IWPb	IWCl	IWSO$_4$
3	65	285	100	4.3	30	71	116	1.80
4	61	32	45	7.2	54	42	42	.22
6	105	50	41	18.4	52	50	56	.51
11	66	140	68	24.0	294	112	100	.98
17	69	21	44	6.0	54	58	42	.84

several kilometers from the outfall. Differences in the concentrations of Cr and Pb in the sediments from sites near the industrial outfall and from sites removed from the outfall were not observed. The greatest difference in the concentration of metals was between the sediment and the drift. Concentrations of metals in the drift were close to three orders of magnitude greater than in the sediments.

Supercritical carbon dioxide fractionated organic matter in the drift samples. Trends were not evident in the amounts of metals that were extracted and did not follow a pattern. The largest amounts of Pb tended to be recovered during the extractions without added modifier at the lowest applied pressure to carbon dioxide. Chromium quantities were the largest in carbon dioxide under pressure greater than 100 atm. Amounts of recovered Cu were the largest at the highest pressures with and without methanol added as a modifier. The FTIR spectra suggest that variation in the supercritical fluid extraction (SFE) extraction conditions results in the extraction of organic compounds with dissimilar functional groups.

DISCUSSION

Of the metals studied, Cu, Cr, and Pb are listed as hazardous metals by the U.S. EPA. All four metals can exist as metallo-organic compounds (Cotton and Wilkinson, 1988). Cu readily forms complexes with organic matter, Pb from manmade sources can enter the environment as an alkyl compound, and reduced Cr readily bonds to nitrogenous organic molecules. The largest concentrations of Pb and Cu in the sediments are found near the outfall canal. It appears that the explanation for these large concentrations of metals in the sediments is the addition of drift from the outfall canal to the sediment of Bayou d'Inde.

The form in which the metal occurs in the ecosystem affects the availability of the metal to biota and to the aqueous phase. If the metal is present as a sulfide, it is retained in the sediment. If the metal is bound to organic matter, it can become part of the food chain or be released to the aqueous phase by microbial activity. The question of whether the contribution of the highly polluted drift to the sediment affects the toxicity of the sediments to test organisms remains unanswered.

To understand the role of heavy metals in the ecosystem, the mode of bonding of the metals to organic matter must be determined. Preliminary data show that, by using SFE fractionation of the organic components of drift samples, the associated metals can be fractionated with organic compounds containing differing functional groups. These data provide evidence that different types of organic bonds retain the metals of interest on the organic matter.

SUMMARY

Drift appears to play an important role in the transport of metals in the area of Bayou d'Inde, a tributary of the Calcasieu River. The concentrations of toxic heavy metals in the drift collected in Bayou d'Inde were far greater than the concentrations in the bed sediments. The largest concentrations of metals in bottom sediment occur in areas nearest the outfall canal. However, the direct contribution of drift to bottom material cannot be established until settling studies of drift have been performed. The role of the free-floating drift in the cycling of metals is not understood; how much becomes a part of the sediments in Bayou d'Inde, and how much is transported to the mainstream of the Calcasieu River?

Preliminary evidence obtained from supercritical fluid extraction of drift samples using carbon dioxide and carbon dioxide modified with methanol at pressure of 100 to 400 atm indicates that the bonds between the metals and the organic matter differ based on functionalities in the organic structure. Metallo-organic complexes that are part of the free-floating drift are labile and subject to degradation by microbial activity. Metals transported in this fashion could become part of the aqueous phase of either the water column or sediment.

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SIGNIFICANCE OF DRIFT AND ORGANIC AND NONORGANIC DETRITUS ON THE MOVEMENT OF SYNTHETIC ORGANIC COMPOUNDS INTO BAYOU D'INDE, LOUISIANA

By Charles R. Demas[1] *and* Dennis K. Demcheck[1]

ABSTRACT

In 1985, the U.S. Geological Survey began a study of the fate and movement of organic contaminants in the lower Calcasieu River Estuary. The estuary, located in southwestern Louisiana, has been heavily affected by numerous chemical industries located along its banks and the banks of its tributaries. The study documented the presence of synthetic organic compounds in the sediments (both bottom and suspended), water, and aquatic organisms in the lower Calcasieu River and one of its tributaries, Bayou d'Inde.

Origins of large concentrations of synthetic organic compounds, especially hexachlorobenzene and hexachlorobutadiene, detected in the bottom material of Bayou d'Inde could not be explained solely by analyses of water and dewatered suspended sediments from Bayou d'Inde. Analyses of drift material, including organic and nonorganic detritus, collected from an industrial outfall canal that empties into Bayou d'Inde showed high concentrations, in the milligrams-per-kilogram range, of these synthetic organic compounds. Field observations indicated that the drift and organic and nonorganic detritus did resettle onto the bottom material which provides a possible explanation for the high concentrations of the compounds. The results indicate that drift and organic and nonorganic detritus, including plant matter and bottom material associated with it, is an important medium for the transport of synthetic organic compounds out of the outfall canal and into Bayou d'Inde.

INTRODUCTION

Many scientists, such as Hynes (1970), have documented the role that drift and organic and nonorganic detritus, defined as both flora and fauna (generated within a flowing water system) which has become detached from its substrate and is suspended in the water column, plays in the movement, behavior, and feeding habits of aquatic organisms. Studies by Darnell (1967), Hynes (1970), and Thurman (1985) have documented the importance of organic detritus in the movement of nutrients in flowing water and estuarine environments. However, the role that drift and organic and nonorganic detritus play in the movement of synthetic organic compounds in aquatic environments has not been well documented.

In 1985, the U.S. Geological Survey (USGS) began a study of the fate and transport of organic contaminants within the lower Calcasieu River Estuary. The estuary, located in southwestern Louisiana, has been affected by numerous chemical industries located along its banks and the banks of its tributaries. Studies by Demas (1988; 1989), Pereira and others (1988), and Demas and Demcheck (1989) documented the presence of synthetic organic compounds in the sediments (both bottom and suspended), water, and aquatic organisms in the lower Calcasieu River and one of its tributaries, Bayou d'Inde.

Studies conducted during 1985-87 (Pereira and others, 1988; Demas, 1989; Demas and Demcheck, 1989) documented the presence of hexachlorobenzene (HCB) and hexachlorobutadiene (HCBD) in bottom material in an outfall canal flowing into Bayou d'Inde. The concentrations of HCB and HCBD, although variable in the studies, were consistently detected at concentrations in the milligrams per kilogram range. Concentrations of HCB and HCBD decreased to the micrograms per kilogram range downstream in Bayou d'Inde and the lower Calcasieu River, and concentrations decreased below detection limits farther downstream. Water analyses from Bayou d'Inde and the outfall canal showed very low concentrations (micrograms per kilogram) of HCB and HCBD present. These low concentrations in water are partly explained by Chiou in Pereira and others (1988), who indicated that the organic compounds detected in the outfall canal and Bayou d'Inde were relatively insoluble in the brackish water present in these two bodies of water.

The concentrations of HCB and HCBD in water and suspended sediment were so low when compared to those in the bottom material that an additional medium of transport was thought to exist. Project personnel noted large clumps of aquatic sedge (in 1986-87) and benthic algae (1990) moving from the outfall canal into Bayou d'Inde. This drift and organic and nonorganic detritus was considered to be a possible mechanism for the transport of HCB and HCBD from the outfall canal into Bayou d'Inde.

This paper presents the results of the analyses of drift and organic and nonorganic detritus, water, suspended sediment, and bottom material from the outfall canal. Plant material, water, suspended sediment, and bottom-material samples were collected in 1986 from an industrial outfall canal, and results of synthetic organic compound analyses were compared to similar data collected in 1990. The data in this report are used to evaluate the role of drift and organic and nonorganic detritus in the transport of synthetic organic compounds. The data are stored in computerized files of the USGS.

MATERIALS AND METHODS

Water, dewatered suspended-sediment, bottom material, and drift and organic and nonorganic samples were collected from a site located near the mouth of an industrial outfall that empties into Bayou d'Inde (fig. 1). Water samples were collected with a wire-basket sampler containing a 1-L (liter) clean, baked, glass bottle. Dewatered suspended-sediment samples were collected

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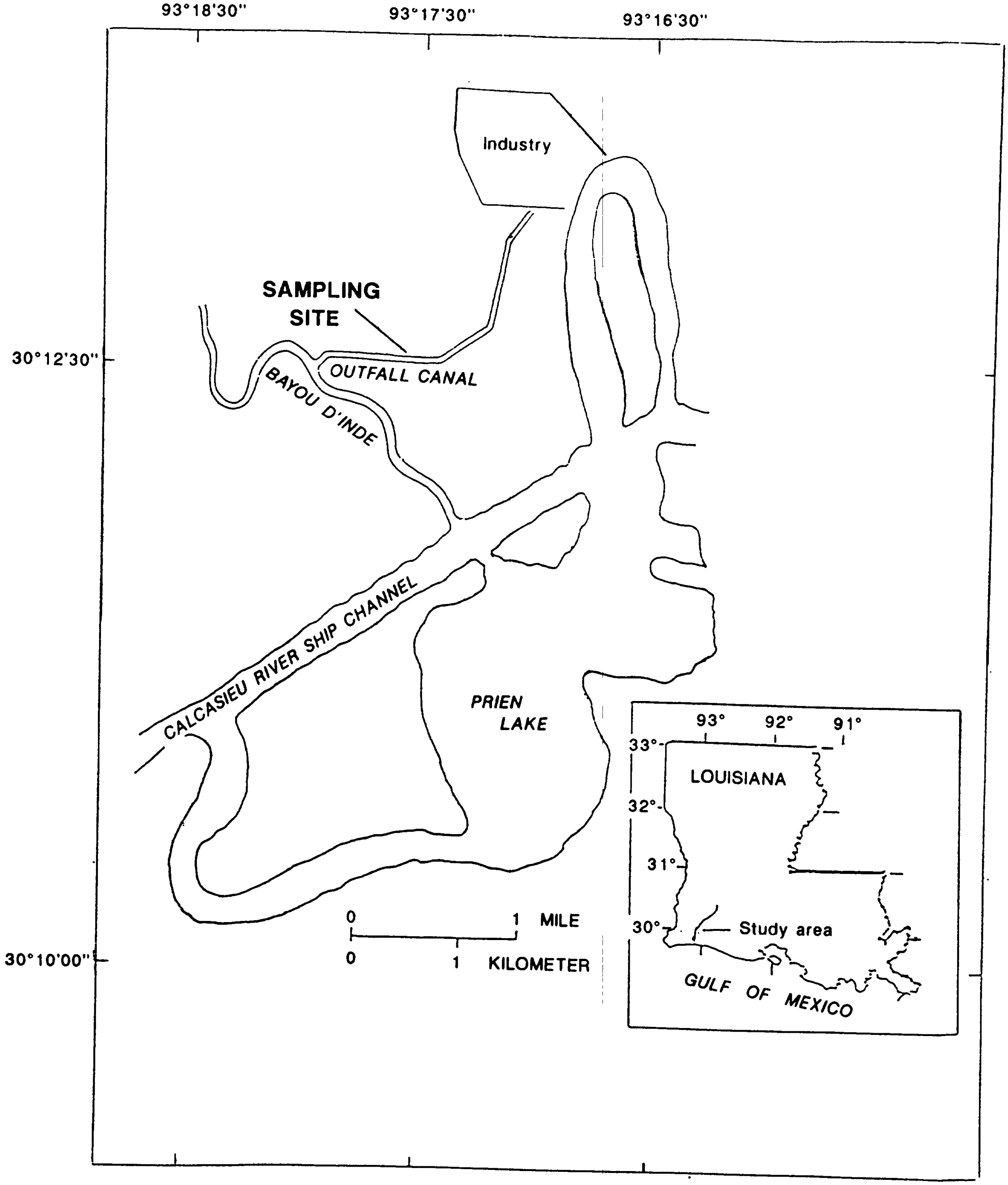
93°18'30"
93°17'30"
93°16'30"
30°12'30"
30°10'00"
Industry
SAMPLING SITE
OUTFALL CANAL
BAYOU D'INDE
CALCASIEU RIVER SHIP CHANNEL
PRIEN LAKE
0 1 MILE
0 1 KILOMETER
93°
92°
91°
33°
32°
31°
30°
LOUISIANA
Study area
GULF OF MEXICO

Figure 1. Study area, Bayou d' Inde.

using a tangential filtration unit with 0.00045 mm (millimeter) filters. The dewatered suspended sediment was removed from the filters and combined with the suspended sediment concentrated in the retentate from the filters. Dewatered suspended sediment was stored in clean, baked, 1-L glass bottles. Bottom material was collected with a stainless-steel petite ponar grab sampler and placed in clean, baked, 1-L glass bottles. Drift and organic and nonorganic detritus samples were collected using a 0.505 mm mesh drift net constructed of nitex sieve material. All samples were chilled to 4 °C (degrees Celsius) immediately after collection. The samples were analyzed for methylene chloride--extractable acid-base/neutral (ABN) compounds.

ABN analyses of 1986 bottom material and suspended sediment were done by a USGS laboratory and ABN analysis of water was done by a Tennessee Valley Authority laboratory according to Method 625 (U.S. Environmental Protection Agency, 1979). ABN analyses of bottom material, suspended sediment, and water collected in July 1990 were done at a USGS laboratory according to methods in Wershaw and others (1983; 1987). Drift and organic and nonorganic detritus samples for both sampling periods were analyzed at Mississippi State University Chemistry Laboratory. Base/neutral compounds were extracted, prepared, and analyzed according to Method 211.1 (U.S. Food and Drug Administration, 1986). Polynuclear aromatic compounds were analyzed using methods developed in cooperation with the U.S. Fish and Wildlife Service (Belisile and others, 1981).

RESULTS OF ANALYSES

Results of ABN analyses of water, dewatered suspended sediment, and bottom material are listed in table 1. Various ABNs were detected at very low concentrations (nanograms per liter) in water samples for both the 1986 and 1990 sampling periods. HCB and HCBD were detected at concentrations of 0.008 and 1.29 µg/L (micrograms per liter) in the 1986 samples and were not detected at all in the 1990 samples. HCB and HCBD were detected in dewatered suspended sediment in 1986 at concentrations of 2.5 and 1.8 mg/kg (milligrams per kilogram). However, when concentrations of HCB and HCBD were adjusted to account for dewatering (from 480 L), concentrations decreased to 5.2 and 3.8 µg/L.

Bottom material, in contrast, contained very high concentrations of ABNs (table 1). For example, HCB and HCBD were detected in concentrations of 350 and 53 mg/kg for coarse-grained bottom material (particles >0.063 mm) in samples collected in 1986 and 302 and 51 mg/kg for coarse-grained bottom-material samples collected in 1990. High concentrations of HCB and HCBD also were detected downstream from the outfall canal in Bayou d'Inde. For example, HCB and HCBD were detected at concentrations of 14 and 4.1 mg/kg, 0.4 km (kilometers) downstream from the outfall canal and 27 and 9.8 mg/kg, 1.6 km downstream.

DISCUSSION

Comparison of the concentrations of HCB and HCBD in suspended sediment and water with concentrations in bottom material indicates some other medium is important in the transport of synthetic organic compounds out of the outfall canal into Bayou d'Inde. This medium appears to be plant drift material and the entrained bottom material that is moving with it. Drift samples collected in 1986 and 1990 had similar concentrations of HCB and HCBD, although the plant material analyzed in the two studies was quite different. In 1986, drift samples were found to contain HCB and HCBD in concentrations of 3.0 and 3.1 mg/kg. Drift samples collected from the outfall canal in 1986 were composed primarily of an unidentified aquatic sedge. In 1990, drift contained HCB and HCBD in concentrations of 1.2 and 1.1 mg/kg. Drift samples collected in 1990 consisted primarily of the blue-green alga *Oscillatoria* sp. The *Oscillatoria* sp. was found to be growing on the bottom of the outfall canal in large mats which periodically detached due to bubbles of photosynthesis-produced oxygen forming within the mats. When these mats detached, they also entrained some of the bottom material.

Drift samples collected in 1986 consisted of a grasslike aquatic sedge. Bottom-material samples from the bayou downstream from the outfallcanal at this time contained large quantities of fibrous organic material that appeared to be quite similar in structure to the material in the drift. This indicates that the drift was settling out of the water column and was being incorporated into the bottom material. Drift samples collected in 1990 appeared to be relatively unstable and the algal mats were observed to break up when artificially agitated or exposed to turbulence. Once broken apart, the mats and associated bottom material appeared to resettle to the bottom of the bayou. In the Bayou d'Inde area, this is most likely to occur when the mats leave the protected waters of the outfall canal and enter Bayou d'Inde.

SUMMARY

Large concentrations of synthetic organic compounds, especially hexachlorobenzene and hexachlorobutadiene, detected in the bottom material of Bayou d'Inde could not be explained solely by analyses of water and dewatered suspended sediments. Analyses of drift material collected at the same time as the bottom material from an outfall canal that flows into Bayou d'Inde showed high concentrations of these synthetic organic compounds. Field observations indicated that the drift was incorporated into the bottom material and was a likely source of synthetic organic compounds to the bed sediments. The results of the study indicate that plant drift and the bottom material associated with it are an important medium for the transport of synthetic organic compounds out of the outfall canal into Bayou d'Inde.

Table 1. *Concentrations of acid-base/neutral organic compounds in water, suspended sediment, bottom material, and plant material in an industrial outfall canal at Bayou d'Inde, Louisiana*

[Water in milligrams per liter; suspended sediment, bottom material, and plant material in milligrams per kilogram; >, greater than; mm, millimeters; <, less than; NA, not analyzed; ND, not detected]

May 1986

Compound	Water column	Suspended sediment	Bottom material Coarse (>0.063 mm)	Bottom material Fines (<0.063 mm)	Drift material
1,3-Dichlorobenzene	0.000048	0.07	3.2	0.57	NA
1,4-Dichlorobenzene	.000074	.09	2.7	.43	NA
1,2,4-Trichlorobenzene	.000040	.37	10	1.6	NA
Hexachlorobenzene	.000008	2.5	350	.73	3.0
Hexachlorobutadiene	.001298	1.8	53	.8	3.1
Octachloronaphthalene	NA	NA	NA	NA	ND
Octachlorostyrene	NA	NA	NA	NA	.66
Benzopyrene	NA	NA	NA	NA	ND
Benzoperylene	NA	NA	NA	NA	ND
Naphthalene	NA	NA	NA	NA	.33
Phenanthrene	NA	NA	NA	NA	ND
Fluoranthene	NA	NA	NA	NA	ND

July 1990

Compound	Water column	Suspended sediment	Bottom material Coarse (>0.063 mm) Duplicates		Bottom material Fines (<0.063 mm)	Drift material Duplicates	
1,3-Dichlorobenzene	ND	ND	26.0	9.6	8.1	NA	NA
1,4-Dichlorobenzene	ND	ND	12.3	4.6	3.8	NA	NA
1,2,4-Trichlorobenzene	ND	ND	6.6	<.2	1.3	NA	NA
Hexachlorobenzene	ND	ND	302.4	235.8	35.0	1.1	1.2
Hexachlorobutadiene	ND	ND	50.8	42.9	12.5	1.1	.91
Benzopyrene	ND	ND	.5	<.4	1.7	.05	.07
Benzoperylene	ND	ND	1.5	<.4	2.6	.05	.08
Naphthalene	ND	0.001	.2	.1	.2	.02	.02
Phenanthrene	ND	.0009	.9	.4	.8	.08	.10
Fluoranthene	ND	.0003	.6	.3	.5	.13	.15

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MIGRATION OF ORGANIC COMPOUNDS THROUGH BED SEDIMENTS NEAR AN INDUSTRIAL OUTFALL IN THE CALCASIEU RIVER ESTUARY, LOUISIANA

By Thomas J. Leiker[1]

ABSTRACT

Studies conducted in the vicinity of an industrial outfall near the Calcasieu River Estuary have shown that the area has been severely affected by the industrial outfall. Water, and sediment samples collected above and below the industrial outfall and at the outfall canal have been shown to be contaminated with a variety of chlorinated, brominated, and mixed chlorinated and brominated benzenes, butadienes, biphenyls, diphenyl ethers, styrenes, dihydro-naphthalenes, and phenols. Concentration of analytes in the water samples varied from nondetectable to 6 ppb parts per billion, and the sediment samples varied from nondetectable to 25 parts per million (dry weight).

Core samples were collected at the outfall and analyzed to study the transport and fate of organic compounds as they migrate through bed sediments. After fractionation into 4-centimeter lengths, the samples were extracted with sonic disruption and analyzed by gas chromatography/mass spectrometry.

INTRODUCTION

Coastal inlets and estuaries that drain into a substantially large body of water are regarded as ideal sites to discharge industrial effluents into the environment. In many instances, the effluents contain hazardous wastes and(or) contain contaminants that initially are not at a hazardous concentration in the aqueous environment, but after a period of time may attain harmful concentrations within bed sediments and stream biota. Discharging industrial wastes into riverine systems has long been considered an acceptable practice to remove unwanted chemical wastes from a chemical plant. This practice has been considered acceptable because the adverse environmental effects of industrial wastes are considered to be minimized by the infinite dilution within a moving body of water. This rationale may be acceptable for contaminants that are water soluble, remain in the aqueous phase, exhibit conservative behavior, have not been shown to be toxic or hazardous, and are removed by the riverine system from the site of the discharge, and do not result in any adverse effects. The rationale becomes questionable when hydrophobic organic contaminants, as well as other anthropogenic compounds, are discharged into or near fragile estuaries or other aquatic systems, and the wastes are not completely removed from the site of the discharge but interact with the bed sediments of the riverine system.

Hydrophobic organic contaminants with large octanol/water partition coefficients (log $K_{ow}4$) selectively partition from the water column into bed and suspended sediments that contain a measurable organic carbon content. Discharges of industrial wastes into these systems may result in a variety of geochemical processes (Brownawell and Farrington, 1986; Ursin, 1985; Duursma, and Dawson, 1981; Sigleo and Hattor, 1985). In some cases, these processes may accelerate the degradation of industrial wastes into forms that have not been identified or into forms for which toxicity data has not been established. These concerns are critical for waters that contain hydrophobic contaminants, because these contaminants can be adsorbed onto the surface of sediments that contain a measurable organic carbon content or partitioned into suspended and bed sediments (Brook and others, 1974; Chiou, 1985), and thereby are allowed to attain elevated concentrations with the bed sediments. At this time, the contaminants can migrate down through the bed sediments, become chemically altered, or become resuspended within the riverine system and become bioavailable or transported on suspended sediments or drift (Darnell, 1967; Hynes, 1970; Thurman, 1985).

The lower Calcasieu River in Louisiana (fig. 1) is part of an estuarine ecosystem that is affected by petrochemical and agrochemical industries (Steinheimer and others, 1981; Pereira and others, 1989). A chemical plant, located near Bayou d'Inde, manufactures trichloroethylene and perchloroethylene (U.S. Environmental Protection Agency, 1975). Effluents from this plant are discharged into Bayou d'Inde. This bayou then drains into the Calcasieu River and finally into the Gulf of Mexico.

In order to better understand the migration and fate of organic compounds as they migrate through sediments, and ultimately afffect quality of ground water, core samples were collected at, above, and below the outfall and, segmented into 4-cm (centimeters) lengths and analyzed by gas chromatography/mass spectrometry(GC/MS).

SAMPLE COLLECTION, EXTRACTION, AND CLEANUP

Briefly, 2 to 3 foot long core samples were collected by driving 2-inch (inside diameter) galvanized pipe into the bed sediment. The cores were extruded in the field or shipped to the laboratory on ice. The top 20 cm of core was divided every 5 cm. The remaining length of core was divided into 4 cm lengths. An aliquot of the core sediment was placed into a 250 mL (milliliter) centrifuge bottle. Surrogate standards consisting of d_{10}-naphthalene and d_{10}-acenaphthene were added to the sample prior to extraction. The sample was extracted for approximately 2 minutes using sonic disruption under pulsed mode, duty cycle of 60 percent, and output setting of 8. The sample was extracted three times with 10 percent acetone in hexane. After each extraction, the sample was centrifuged for 10 minutes at 1,500 RP. The extracts were combined and dried over Na_2SO_4. The extracts were

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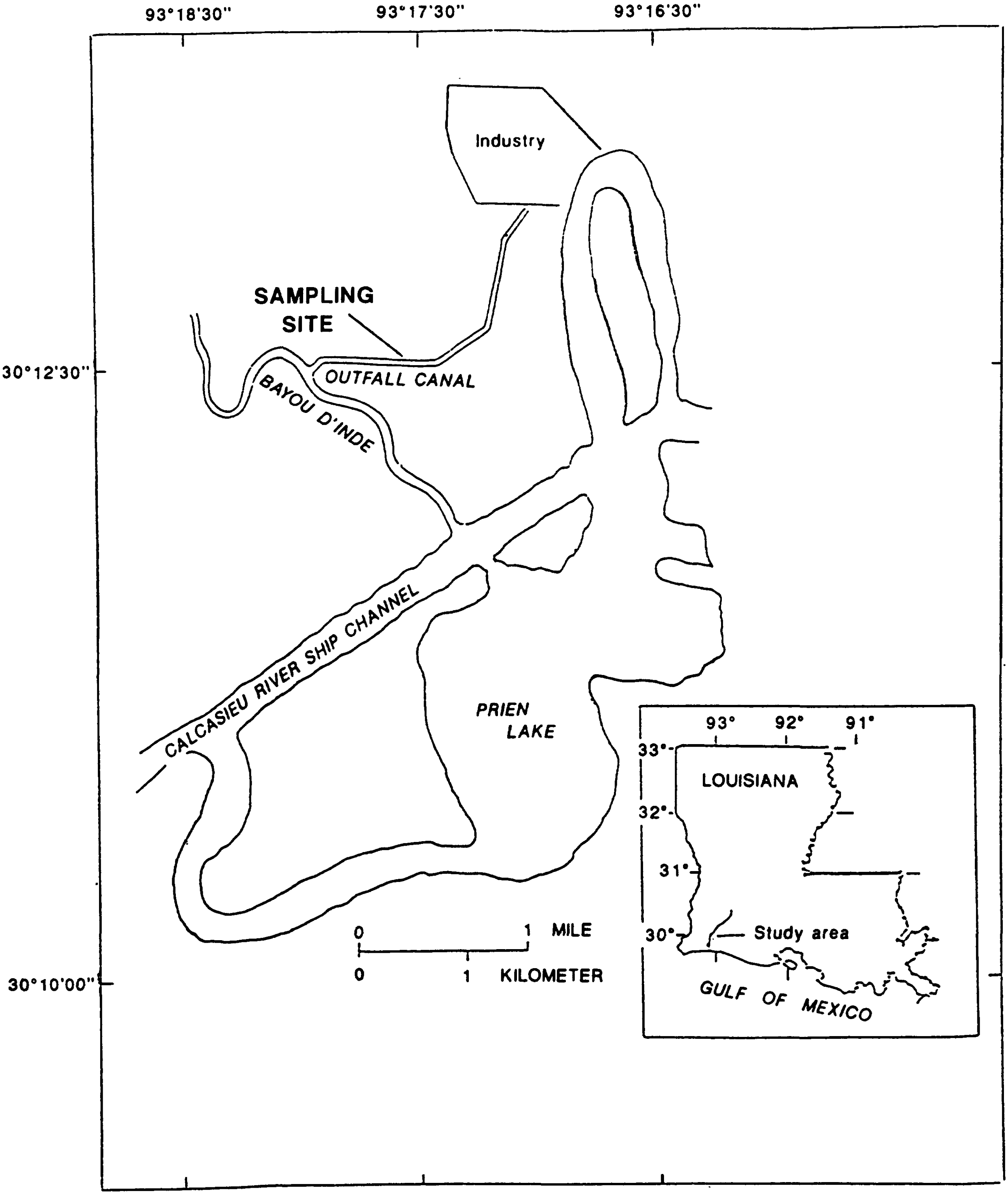
93°18'30"
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93°16'30"
30°12'30"
30°10'00"
Industry
SAMPLING SITE
OUTFALL CANAL
BAYOU D'INDE
CALCASIEU RIVER SHIP CHANNEL
PRIEN LAKE
0 1 MILE
0 1 KILOMETER
93° 92° 91°
33°
32°
31°
30°
LOUISIANA
Study area
GULF OF MEXICO

Figure 1. Study area, Bayou d'Inde.

concentrated and purified by passage through a microflorisil column that contained a layer of activated copper for removal of sulfur. The column was eluted with 25 mL of 10 percent diethyl ether in hexane. After elution from the column, the purified extract was concentrated under a gentle stream of nitrogen to a volume of 100 microliter. The extract was sealed and stored at 4 °C until analysis by GC/MS.

RESULTS AND DISCUSSION

Selected hydrophobic organic contaminants that have been identified in the core samples are listed in table 1. The highest contaminant levels were detected in sediment from the outfall channel. The concentrations ranged from 0.5 µg/g (micrograms per gram) to 25 ug/g dry weight. The concentrations of contaminants in the sediments downstream of the outfall ranged from non-detectable to approximately 7 µg/g dry weight. Sediment samples upstream of the outfall contain detectable levels of contaminants, but are lower in concentration than either the outfall or downstream of the outfall. These results indicate that the Calcasieu River Estuary has been adversely affected by indistrial discharges from the chemical industry that is located along its banks.

Table 1. Selected hydrophobic organic compounds that have been identified in core samples from the Calcasieu River Estuary

Dichlorobenzenes
Trichlorobenzenes
Tetrachlorobenzenes
Pentachlorobenzene
Hexachlorobenzene
Hexachlorobutadiene
Dichlorostyrenes
Tetrachlorostyrenes
Pentachlorostyrenes
Hexachlorostyrenes
Heptachlorostyrenes
Octachlorostyrene
Dibromodiphenyl ethers
Trichlorophenols
Tetrachlorophenols
Pentachlorophenols
Nonachlorobiphenyls
Decachlorobiphenyl
Octachlorodiphydronaphthalenes
Decachlorodiphydronaphthalene

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EFFECTS OF GEOCHEMICAL FACTORS ON REMOBILIZATION AND REDEPOSITION OF CONTAMINATED BED SEDIMENTS IN BAYOU D'INDE, LOUISIANA

By Kurt L. Johnson[1] *and* Jerry A. Leenheer[2]

ABSTRACT

Contaminated bed sediment from Bayou d'Inde, a tributary of the lower Calcasieu River, was elutriated with water of different salinities to determine the effects of geochemical factors on remobilization and redeposition of sediment. As the salinity decreased from 3.0 to 0.2 parts per thousand, the amount of suspended sediment forming stable colloidal suspensions increased from 0.06 to 8.27 percent. Colloid mineralogy was predominately quartz at 3.0 parts per thousand salinity. At 0.2 parts per thousand salinity, the mineralogy changed to predominately smectite, with lesser quantities of kaolinite, illite, and quartz. At 0.2 parts per thousand salinity, concentrations of halogenated organic compounds in resuspended sediments generally were lower than the concentrations in the remaining bed sediment.

INTRODUCTION

Bayou d'Inde is a small tributary of the lower Calcasieu River, located in southwestern Louisiana (fig. 1). Bed sediment in this small, generally brackish, bayou contains concentrations of halogenated organic compounds that decrease downstream from an industrial outfall canal (Pereira and others 1988; Demas and Demcheck, 1989). These compounds have a strong affinity to sediments, as shown by their relatively large octanol-water partition coefficients (Kow). Pereira and others (1988), using laboratory methods developed by Chiou and others (1982), reported that Kow values were about 20 percent higher in brackish water and saltwater than in distilled water.

Pereira and others (1988), Demas and Demcheck (1989), and J.A. Leenheer and T.I. Noyes (U.S. Geological Survey, written commun., 1990), expressed concern about the effects of dredging and storm runoff on the transport and fate of contaminants in the Bayou d'Inde area. To gain additional knowledge about remobilization of contaminants, a laboratory study was conducted by the U.S. Geological Survey (USGS) to verify field results and present a more accurate assessment of the potential for remobilization of organic contaminants from bed sediments during freshwater inflows.

This paper describes the results of the laboratory study of the effects of the geochemical factors of salinity, clay mineralogy, and organic content of bed sediments from Bayou d'Inde on the potential for contaminant remobilization, and redeposition. Bed sediment samples were resuspended in saline water to simulate turbulence in Bayou d'Inde, using a modified elutriate method. Data are stored in files of the USGS.

MATERIALS AND METHODS

In April 1989, 10 liters of bed sediment from Bayou d'Inde at the mouth of an industrial outfall canal were collected, (Demas and Demcheck, 1989), composited, and stored at 4 °C (degrees Celsius) until processed at a USGS laboratory. A brass 250-micrometer sieve was used to remove organic detritus and other foreign materials from the samples, using a minimal amount of artificial seawater prepared according to Hem (1985).

A modified elutriate method (Keeley and Engler, 1974) using saline water was used to simulate resuspension of bed sediments under turbulent conditions. A 1:4 gravimetric ratio of sediment to water was stirred and allowed to settle for 24 hours. Sediment remaining in suspension was dewatered by centrifugation, freeze-dried, and weighed.

Preliminary analyses for organic carbon concentration and clay mineralogy of suspended sediment were determined by infrared spectrometry. Organic carbon concentration of suspended and bed sediment was determined by a private laboratory.

Median particle-size determinations were made using photon correlation spectroscopy. A USGS laboratory determined the clay mineralogy by X-ray diffraction. Concentrations of synthetic organic chemicals were analyzed using solvent extraction followed by gas chromatography-mass spectrometry (Pereira and others, 1988).

RESULTS

Chemical and physical properties of waters and sediments from the elutriate experiments are presented in table 1. The amount of suspended sediment was inversely proportional to the salinity of the elutriating water. The mass median particle sizes of suspended sediment fractions as a function of salinity were relatively consistent; the 24-hour periods of settling resulted in a comparable particle size. Sediments that remained in suspension with waters up to 1.0 ppt (part per thousand) salinity were depleted in organic carbon relative to the bed sediment before elutriation. Sediments suspended with 2.0- to 3.0-ppt salinity waters were enriched in organic carbon.

The infrared spectra of suspended sediment obtained from the elutriation experiments as a function of increasing salinity are shown in figure 2. A significant change was observed in the mineralogy of the suspended sediments between salinities of 1.0 and 2.0 ppt. Hydrous clay peaks at 3,655, 3,625, and 1,035 cm^{-1} (per centimeter) dominated the

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[1] U.S. Geological Survey, Baton Rouge, La.

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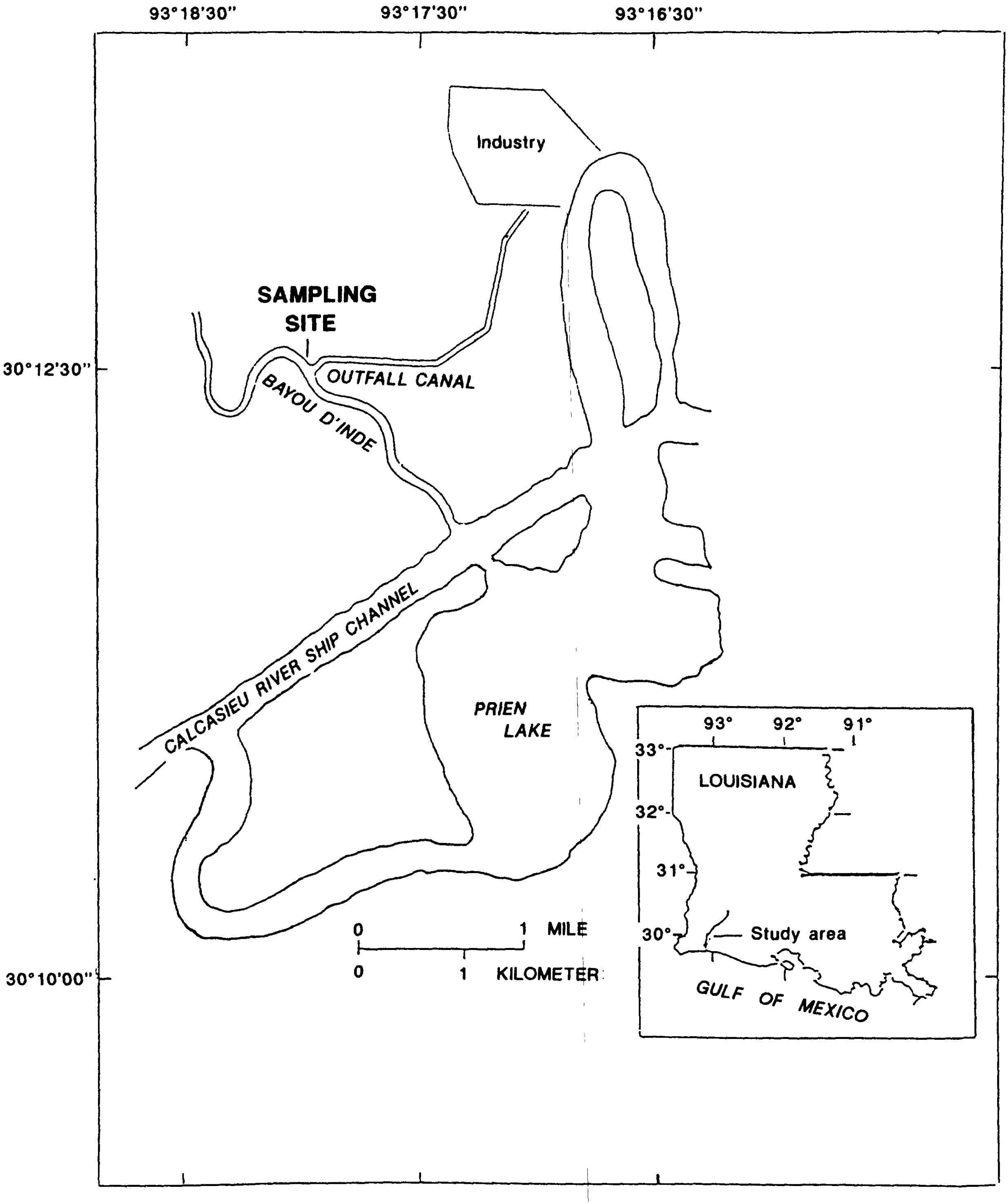
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93°17'30"
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Industry
SAMPLING SITE
OUTFALL CANAL
BAYOU D'INDE
CALCASIEU RIVER SHIP CHANNEL
PRIEN LAKE
0 1 MILE
0 1 KILOMETER
93°
92°
91°
33°
32°
31°
30°
LOUISIANA
Study area
GULF OF MEXICO

Figure 1. Location of study area, Bayou d' Inde.

infrared spectra for sediments suspended by 0.2, 0.6, and 1.0 ppt salinity water. The peak at 1,095 cm^{-1} and the double peak near 800 cm^{-1} for the sediments suspended by the 2.0 and 3.0 ppt salinity water indicated a shift in mineralogy from hydrous clay to quartz colloids. This order of mineralogy fractionation with salinity parallels the mineralogical order of deposition of suspended sediments in a number of estuaries (Edzwald and O'Melia, 1975; Whitehouse and others, 1960).

The data in table 1 indicate that significant amounts of suspended sediment from the elutriation experiments occurred at salinities of less than 2.0 ppt. To obtain additional mineralogy information on these sediments, X-ray diffraction was performed before and after expansion of certain clays with ethylene glycol. The X-ray diffractograms after glycolation are shown in figure 3. About 70 percent of the mixed-layer, illite-smectite clays, were found to be expandable after glycolation for sediments suspended by 0.2 ppt salinity water; this percentage decreased to near 60 percent for sediments suspended by 0.6 ppt salinity water. As the proportion of peak intensities for illite, kaolinite, and quartz is nearly constant for the two diffractograms in figure 3, the increase in peak intensities in figure 3A compared to figure 3B for the illite-smectite peaks near 5° 2Θ and the quartzillite, smectite peaks near 27° 2Θ results from an increase in expandable smectite.

Synthetic organic compounds associated with sediment fractions obtained in the elutriation experiments are presented in table 2. The same synthetic organic compounds were detected at concentrations comparable to those reported by Pereira and others (1988). Some of the concentrations are difficult to explain because of analytical

Table 1. *Chemical and physical properties of waters and sediments after elutriation in distilled and saline water*

[Concentration of saline water in ppt, parts per thousand; μS/cm, microsiemens per centimeter at 25 degrees Celsius; μm, micrometer]

Sample[1]:	Sediment in distilled water		Sediment suspended in saline water			
	Suspended	Settled	0.5	1.0	2.0	3.0
Specific conductance, μS/cm, of water after elutriation	280	280	750	1,250	2,550	3,550
Salinity, ppt, of water after elutriation	.2	.2	.6	1.0	2.0	3.0
Percent of suspended sediment after elutriation	8.27	(2)	1.72	.97	.04	.06
Mass median particle size, μm	(3)	(3)	.36	.37	.36	.25
Percent organic carbon of sediment	(4)	3.61	1.93	1.91	3.31	4.09

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[1] Bed sediment before elutriation had 2.37 percent organic carbon.

[2] Not applicable.

[3] Nondetectable.

[4] Not analyzed.

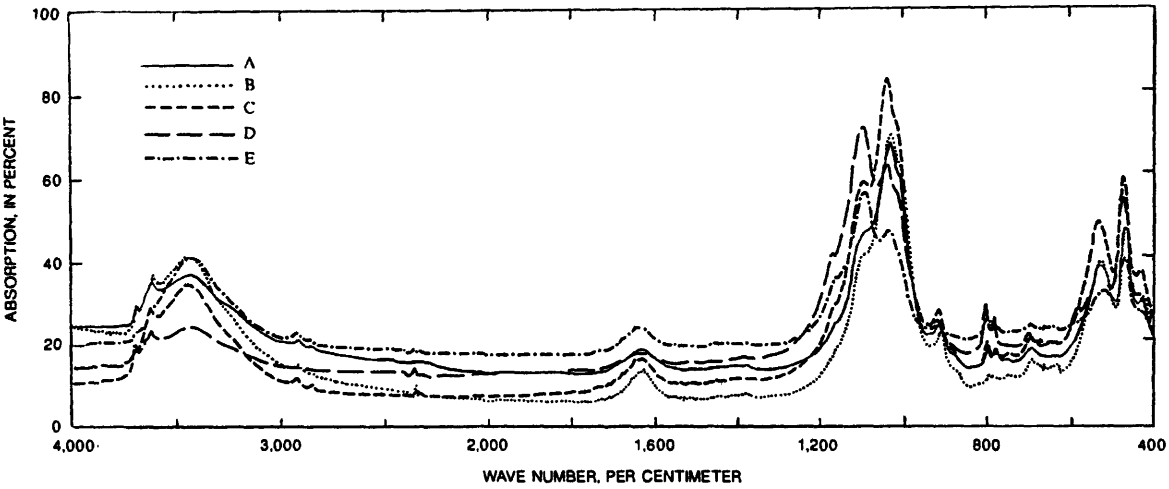

Figure 2. Infrared spectra of suspended sediment fractions from elutriation of Bayou d' Inde bed sediments with water of salinities in parts per thousand of (A) 0.2, (B) 0.6, (C) 1.0, (D) 2.0, and (E) 3.0.

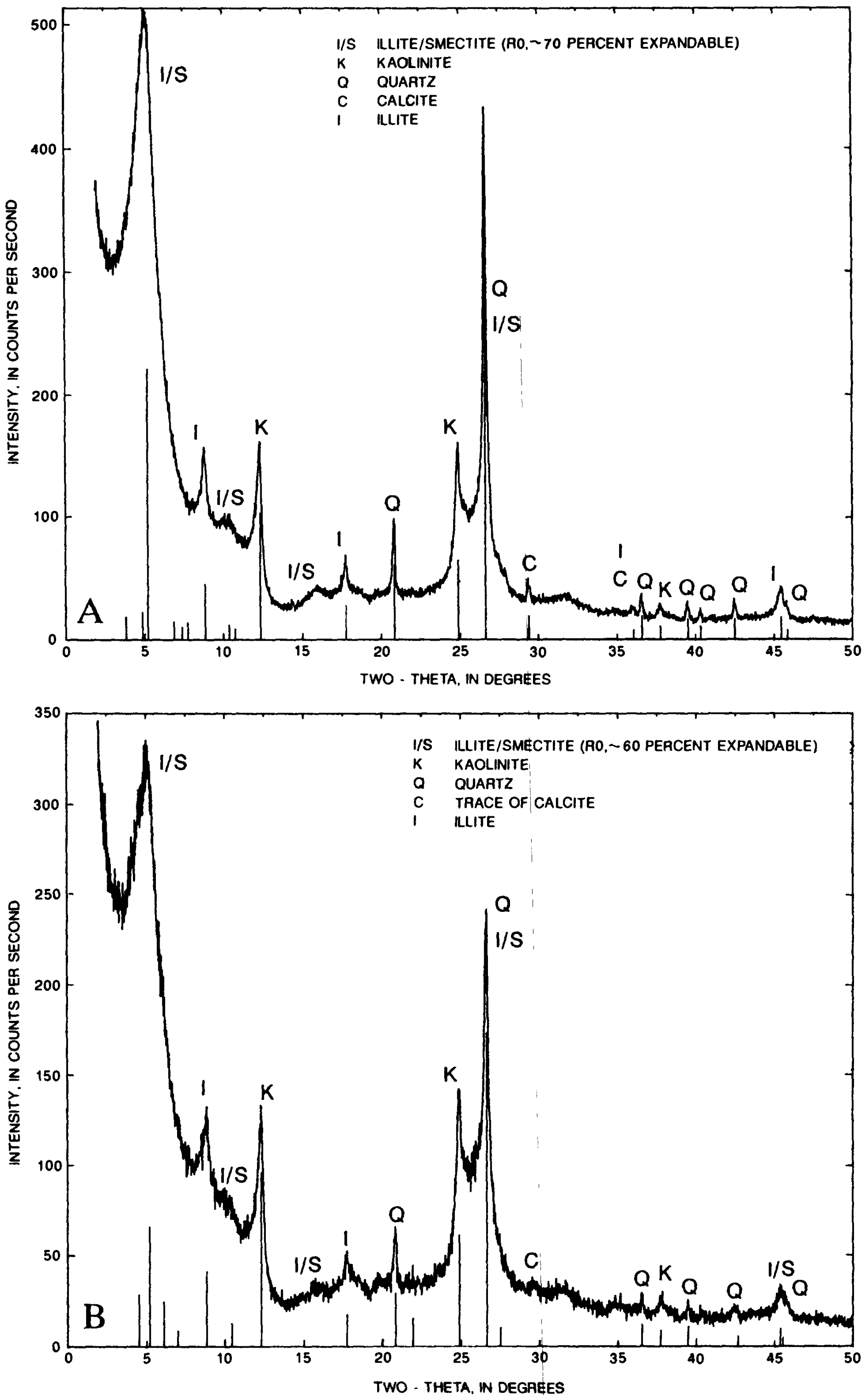

Figure 3. X-ray diffractograms of suspended-sediment fractions from elutriation of Bayou d' Inde bed sediments with waters of salinities in parts per thousand of (A) 0.2 and (B) 0.6.

Table 2. *Concentrations of halogenated organic compounds in sediment fractions from elutriation of Bayou d'Inde bed sediments*

[Concentration of saline water in parts per thousand; concentrations are in micrograms per gram]

	Sediment suspended by saline water		Sediment settled in saline water
	0.6	0.2	0.2
1,3-Dichlorobenzene	1.0	1.6	13.6
1,4-Dichlorobenzene	.9	1.1	8.6
1,2-Dichlorobenzene	2.5	.1	.9
1,3,5-Trichlorobenzene	1.4	2.0	11.2
1,2,4-Trichlorobenzene	4.9	5.6	35.7
1,2,3-Trichlorobenzene	.5	.5	1.0
1,2,4,5-Tetrachlorobenzene	4.7	5.9	15.7
1,2,3,4-Tetrachlorobenzene	1.0	1.4	5.0
Pentachlorobenzene	13.7	18.5	36.7
Hexachlorobenzene	36.9	48.6	103.5
Hexachloro-1,3-butadiene	8.8	9.1	39.6
Octachlorostyrene	36.2	41.4	32.4
Octachloronaphthalene	51.9	54.6	42.0

difficulties with extractions. Generally, the concentrations of synthetic organic compounds in the settled bed sediment are greater than the concentrations in the suspended sediment fractions. This difference is predicted by the greater concentrations of organic carbon (table 1) in the settled bed sediment compared to the suspended sediment.

Natural organic matter is known to be an important constituent in promoting the flocculation of suspended sediments in estuarine waters (Eisma, 1986). In Bayou d'Inde sediments, the concentrations of synthetic organic compounds may be so great that the organic compounds themselves may promote the flocculation and deposition of bed sediments. However, if Bayou d'Inde sediments are resuspended in low salinity waters during a storm, the charge-stabilized colloid suspensions that result will serve as a medium to transport organic compounds to other parts of the lower Calcasieu River, and ultimately into the Gulf of Mexico.

There is a large quantity of detritus from swampgrasses and woodchips in bed sediment that contains significant quantities of synthetic organic compounds (W.E. Pereira, U.S. Geological Survey, oral commun., 1990). The detritus and woodchips may be an important medium for transport of these compounds. A separate study may be needed to evaluate the transport characteristics of organic detritus and woodchips in the lower Calcasieu River because their transport characteristics differ from those of colloids.

SUMMARY

The elutriate samples indicate that geochemical factors such as salinity, clay mineralogy, and organic carbon affect the remobilization (resuspension) and redeposition of synthetic organic chemicals in Bayou d'Inde, Louisiana. Stable colloid suspensions were produced in significant amounts when the salinity of the water was less than 2.0 ppt. Only quartz colloids were stable when the salinity was 2.0 and 3.0 ppt. As the salinity was decreased from 3.0 to 0.2 ppt, kaolinite and illite went into suspension, and expandable smectite clays, which accounted for the greatest mass increase, went into suspension below 0.6 ppt salinity.

Compared to the original bed sediment, the resuspended sediment obtained with low salinity waters indicated lower percentages of organic carbon and synthetic organic compounds. Because natural organic matter promotes flocculation of suspended sediments in estuarine waters, the concentrations of synthetic organic compounds may promote flocculation and deposition in Bayou d'Inde. Also, stable colloidal suspensions from resuspended sediment in low salinity water can transport organic compounds. The organic detritus that was removed from the sediments may be a more important medium for transport of organic compounds than transport on sediment colloids.

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EFFECT OF THE UNSATURATED ZONE ON THE MIGRATION AND RETARDATION OF A CONSERVATIVE TRACER AT THE PLAINS, GEORGIA, RESEARCH SITE

By D.W. Hicks[1], J.B. McConnell[1], *and* R.K. Hubbard[2]

ABSTRACT

Data collected at a 2-acre research plot (planting area) were used to define and evaluate the factors that control the fate and transport of conventionally applied agrichemicals. It was hypothesized that the heterogeneity in hydraulic conductivity of the unsaturated zone has a substantial effect on the rates of infiltration and in the transport pathways of solute.

The results of the investigation suggest that the lateral transport of a conservative tracer (potassium bromide solute) may be a substantial component of its dispersion in the unsaturated zone. Data from this investigation indicate that soil heterogeneity substantially affects the migration rates and pathways of surface-applied chemicals and that one-dimensional (vertical) transport in the unsaturated zone is rare and may be observed only where the soil column is homogeneous and permeable. The lateral migration of solute at the interface between permeable and less permeable material may account for a large part of the dispersion of agrichemicals in the unsaturated zone. Moreover, the lateral rate of movement may be greater than that observed in the vertical.

At the study site, atrazine, alachlor, carbofuran, and the conservative tracer were uniformly applied over the planting area in June 1989, and since application, more than 4,000 soil samples were collected for chemical analysis to evaluate the rates of degradation and transport. Analytical results indicate that, during the first 70 days after application, the center of mass of bromide infiltrated to a depth of about 48 inches in the planting area. From 70 to 350 days, the infiltration rate of the bromide mass was retarded at a depth of about 54 inches in the northeastern part of the area, but the tracer continued to infiltrate vertically to a depth of about 114 inches in the southwestern part of the area. In addition, the total bromide mass in the soil column progressively decreased over time in the northeast and increased in the southwest; thus indicating that the bromide mass within the planting area was migrating laterally from the upslope area.

The apparent anomolies in the migration of the bromide tracer are directly related to characteristics of hydrogeology in the planting area. The northeastern (upslope) part of the planting area is characterized by a shallow, 8-feet-thick layer of dense clay having an average vertical hydraulic conductivity of 0.36 feet per day. The upper part of the clay layer is extremely dense at a depth of about 4 to 5 feet, and in laboratory infiltration tests, would not allow water to pass (vertical hydraulic conductivity estimated to be 0.01 foot per day). Downslope, in the southwestern part of the area, the unsaturated zone is characterized by clean, quartz sand and a higher vertical hydraulic conductivity (1.02 - 5.03 feet per day). Between the northeastern and southwestern parts of the planting area is a transition zone having intermediate lithologies and vertical hydraulic conductivities.

INTRODUCTION

The vulnerability of ground water to contamination by agrichemicals is relatively high in several regions of the United States, particularly in the corn-belt region of the Midwest and the Coastal Plain of the Southeast. Heavy use of chemicals on farmlands in these regions increases the potential for nonpoint source contamination of the water resources. A cooperative, interdisciplinary research investigation in a ground-water recharge area near Plains, Ga., was initiated in 1986 by the U.S. Geological Survey (USGS), U.S. Department of Agriculture, Agricultural Research Service (ARS), and U.S. Environmental Protection Agency (USEPA) to improve current understanding of the complex processes that control the transport and fate of atrazine, alachlor, carbofuran, and a conservative tracer (potassium bromide) in the soil-root, unsaturated, and saturated zones. To develop this improved understanding, it was necessary to define the spatial variability of the hydrogeologic properties, to define environmental factors that control the transport and fate of agrichemicals, and to evaluate the physical and chemical processes that are important to the validation and testing of solute-transport models. This paper describes the results of a part of this investigation.

The heterogeneity in hydraulic conductivity of the unsaturated zone was hypothesized to have a substantial effect on the rates of infiltration and in the transport pathways of solute. The vertical position of the center of mass of a conservative tracer at a specific time is a relative indicator of the infiltration potential of the soil medium. Although other environmental and physical factors may affect the acceleration or retardation of the tracer, it should not be sorbed to soil particles because it is conservative. Thus, the vertical saturated hydraulic conductivity is assumed to be the predominant controlling factor for the migration of the tracer.

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). The area includes two, 16.7-acre farm fields and approximately 40 acres of adjacent woodland--a total of 73.4 acres (fig. 1). The fields are in an interstream area that separates two, small watersheds. The area is characterized by a relatively level cultivated tract having wooded midslope and toe-slope areas extending to the adjacent streams. Altitudes range from

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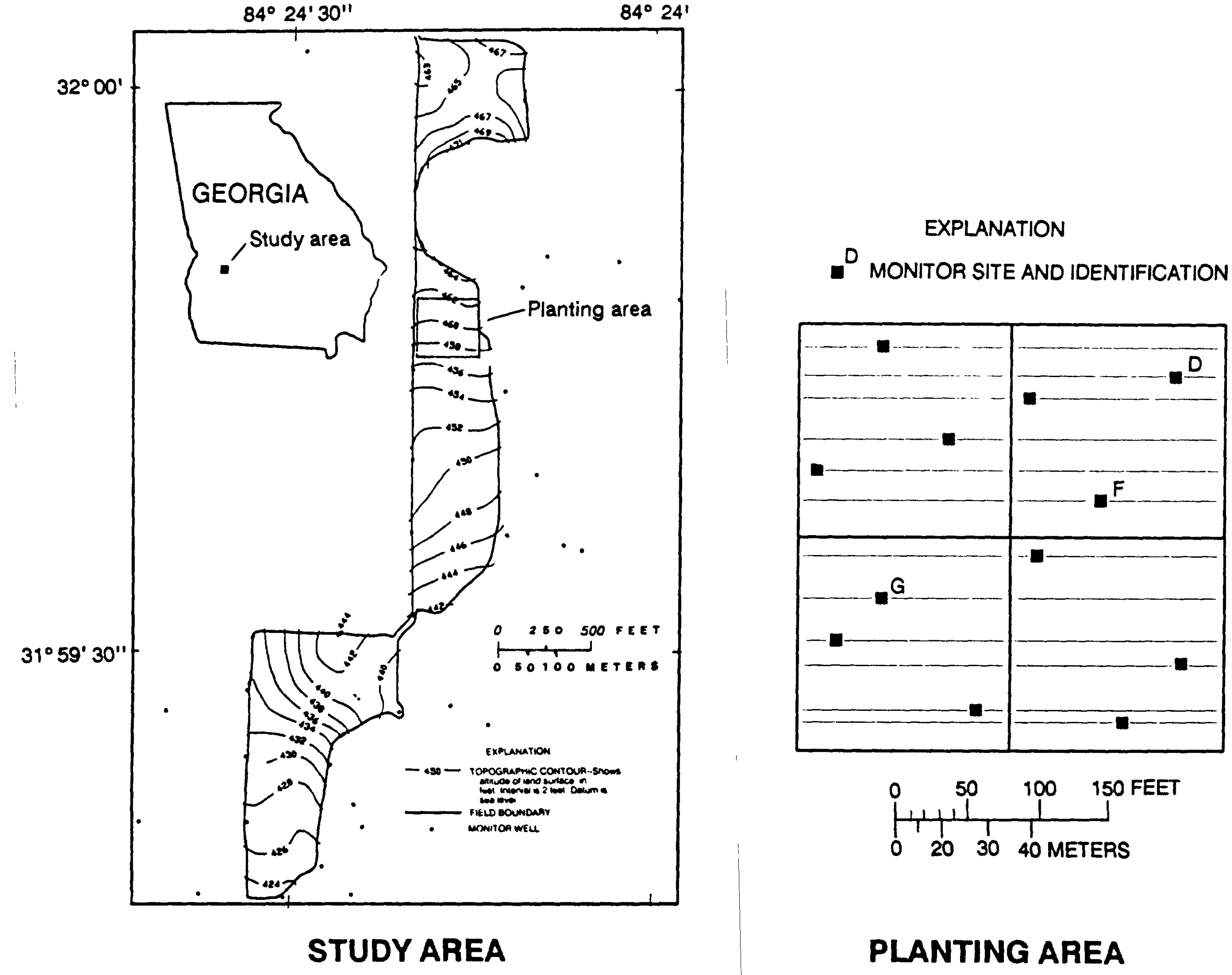
[1] U.S. Geological Survey, Doraville, Ga.
[2] U.S. Department of Agriculture, Agricultural Research Service, Tifton, Ga.

about 390 to 470 ft (feet) above sea level. Interior drainage is typical of the area, resulting from sandy, highly permeable, surface soils. A 2-acre planting area (300 by 290.4 ft) was delineated within one of the 16.7-acre fields and instrumented. Altitudes in the planting area range from about 458 to 462 ft above sea level.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84° 24'
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GEORGIA
Study area
Planting area
0 250 500 FEET
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EXPLANATION
430 TOPOGRAPHIC CONTOUR--Shows altitude of land surface in feet. Interval is 2 feet. Datum is sea level
FIELD BOUNDARY
MONITOR WELL
STUDY AREA
EXPLANATION
D MONITOR SITE AND IDENTIFICATION
D
F
G
0 50 100 150 FEET
0 20 30 40 METERS
PLANTING AREA

Figure 1. Location of study area, planting area, and monitor sites in the planting area.

The hydrogeologic units of importance to this study are, in descending order (1) the undifferentiated overburden, consisting of alternating and intermittent layers of sand, clayey sand, and clay; (2) the Tallahatta Formation (in the Claiborne Group), composed of fine-to-coarse, quartz sand; and (3) the Tuscahoma Formation, which consists of homogeneous, well sorted, glauconitic, very fine-to-fine, argillaceous, quartz sand.

The unsaturated zone includes the undifferentiated overburden and the upper part of the Tallahatta Formation, and ranges in thickness from about 26 to 30 ft. The saturated zone (Claiborne aquifer) is restricted to the lower part of the Tallahatta Formation and ranges in thickness from about 8 to 15 ft in the planting area. It is underlain by the Tuscahoma Formation and generally is unconfined.

Method of Study

Permanent monitoring stations are located randomly at 12 sites in the 2-acre planting area (fig. 1). At each of the 12 sites, continuous, undisturbed soil core were collected from land surface to the saturated zone. Saturated hydraulic conductivity was determined for sections of the soil core in the laboratory by using a falling-head, flexible-wall permeameter. Subsamples of the soil core were analyzed to determine pretreatment concentrations of agrichemical residues and potassium bromide.

Subsequent to tilling and fertilization, corn was planted during June 1989, and atrazine, alachlor, carbofuran, and potassium bromide were applied, in liquid form. The pesticides were applied in accordance with recommended rates provided by each manufacturer. A quantity of 277 lbs (pounds) of potassium bromide salt, or 186 lbs of bromide, was uniformly applied over the planting area as a conservative tracer.

To evaluate the rate of migration and the fate of the compounds applied in the planting area, more than 4,000 soil samples were collected since June 1989. Soil/pore water extracts were removed from the samples and bromide determinations were made by using an ion chromatograph. For each sampling period, a vertical profile of the bromide distribution was developed as well as a computation of the center of mass and total of mass. Thus, a record has been maintained since application of the relative position of the bromide mass and total bromide in the soil column at selected time periods over the entire plot area.

RESULTS

Results of soil-core analyses, borehole geophysical logging, and ground-penetrating radar surveys indicate that the lithology and hydraulic characteristics of the unsaturated zone are heterogeneous and vary substantially over a small area. The northeastern part of the planting area occupies the topographic high position and is the crest of the drainage divide separating the two watersheds. This part of the planting area is underlain by unconsolidated sediments that are dominated by an 8-ft-thick layer of dense clay that extends from a depth of about 3 to 11 ft below land surface. At site D, in the northeastern part of the planting area, the saturated vertical hydraulic conductivity of the clay layer averages about 0.36 ft/d (feet per day). In this area, the saturated vertical hydraulic conductivity ranges from 0.01 ft/d at a depth of about 5 ft, to 4.91 ft/d at a depth of about 26 ft. Downslope in the southwestern part of the planting area at site G, the clay layer is absent and the sediments are characterized by relatively clean, medium quartz sand. In this area, the vertical hydraulic conductivity ranges from 1.02 ft/d at a depth of about 7 ft, to 5.03 ft/d at a depth of about 23 ft. Between the northeastern and southwestern parts of the planting area is a transition zone with intermediate lithologies and vertical hydraulic conductivities.

Analyses of bromide concentrations indicate that during the first 70 days after application the center of mass of the bromide tracer migrated to a uniform depth of about 48 in. (inches) below land surface at sites D, F, and G (fig. 2). The total mass of bromide was uniform in the soil columns (table 1).

Table 1. *Total bromide mass in the soil columns during the 350-day period since application*

[μg, micrograms; NS, not sampled]

Site	Time since application (days)	Bromide, in soil column (μg)
D	70	948
	145	938
	225	473
	350	258
F	70	860
	145	784
	225	1,543
	350	NS
G	70	899
	145	1,302
	225	785
	350	1,423

From 70 to 145 days after application, the bromide remained at about the same depth in the northeastern part of the plot at site D and progressively increased in depth during migration downslope (fig. 2). After 145 days, the center of mass of bromide in the southwestern part of the planting area at site G was at a depth of 72 in. Total mass of bromide remained nearly uniform.

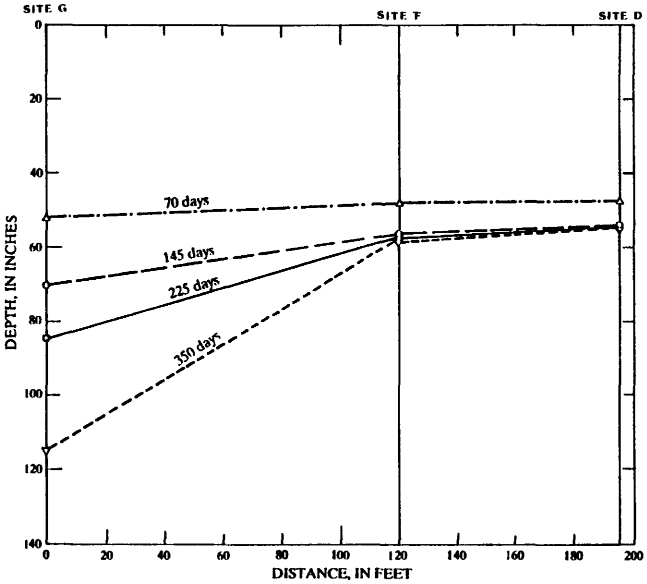

Figure 2.--Bromide distribution in the unsaturated zone 70, 145, 225, and 350 days after application.

Figure 2. Bromide distribution in the unsaturated zone 70, 145, 225, and 350 days after application.

Samples collected 225 days after application indicated that the center of mass had moved slightly downward at site D, but had moved significantly downward at site G. More importantly, the total bromide mass had decreased at site D from about 950 μg (micrograms) to less than 500 μg. In the transition zone at site F, the total bromide mass had increased from 860 μg to more than 1,500 μg (table 1).

Analyses of samples collected 350 days after application indicated that the vertical position of the bromide at site D was nearly unchanged (approximately 60 in. below land surface); however, the total mass of bromide had decreased to about 250 μg (fig. 2 and table 1). At site G, the center of mass had migrated to a depth of about 120 in., but, more importantly, the total mass of bromide in the soil column at that site had nearly doubled since the previous samples were collected.

SUMMARY AND CONCLUSIONS

This study was conducted as a part of a cooperative research project underway since 1986 near Plains, Ga., in the Fall Line Hills district of the Coastal Plain physiographic province of southwestern Georgia in Sumter County. The USGS, ARS, and USEPA instrumented a 2-acre research plot (planting area) to define and evaluate the factors that control the fate and transport of conventionally applied agrichemicals. It was hypothesized that the heterogeneity in hydraulic conductivity of the unsaturated zone has a substantial effect on the rates of infiltration and in the transport pathways of solute.

The hydrogeology of the unsaturated zone is heterogeneous and varies substantially over a small area. The northeastern part of the planting area is characterized by a shallow, 8-ft-thick, layer of clay having relatively low vertical hydraulic conductivity (average, about 0.36 ft/d). The southwestern part of the area is characterized by clean, medium quartz sand. Here, the vertical hydraulic conductivity ranges from 1.02 to 5.03 ft/d. Between the northeastern and southwestern parts of the planting area is a transition zone having intermediate lithologies and vertical hydraulic conductivities.

Subsequent to tilling and fertilization, corn was planted during June 1989, and atrazine, alachlor, carbofuran, and a conservative tracer (potassium bromide) were applied, all in liquid form, and since application, more than 4,000 soil samples have been collected for chemical analysis to evaluate the rates of degradation and transport of the applied chemicals. The results indicate that, during the first 70 days after application, the center of mass of bromide infiltrated to a depth of about 48 in. From 70 to 350 days, the infiltration rate of the bromide mass was retarded at a depth of about 54 in. in the northeastern part of the area. However, in the southwestern part of the area, the tracer continued to infiltrate vertically and was at a depth of about 114 in. In addition, the total bromide mass in the soil column progressively decreased with time in the northeast and increased in the southwest.

Preliminary results suggest that the lateral transport of the bromide solute may be a substantial component of its dispersion in the unsaturated zone and that soil heterogeneity significantly affects the migration rates and pathways of surface-applied chemicals. Moreover, one-dimensional transport in the un saturated zone is rare and may be observed only where the vertical soil column is homogeneous and permeable. The lateral migration of solute at the interface between permeable and less permeable material may account for a large part of the dispersion of agrichemicals in the unsaturated zone. Also, the rates of movement may be greater in the lateral than observed in the vertical.

APPLICATION OF THE GLEAMS MODEL AT THE PLAINS, GEORGIA, AGRICULTURAL-MANAGEMENT SITE

By R. A. Leonard[1], W. G. Knisel[1], F. M. Davis[1], *and* C. C. Truman[1]

ABSTRACT

In 1988, the U.S. Geological Survey; the U.S. Department of Agriculture, Agricultural Research Service; the U.S. Environmental Protection Agency, and the University of Georgia began a cooperative study of chemical transport in a representative agricultural management system near Plains, Georgia. A major objective was to establish data bases for interagency model testing and evaluation. The U.S. Department of Agriculture team of the Southeast Watershed Research Laboratory, Tifton, Georgia, through development and testing of the GLEAMS (Groundwater Loading Effects of Agricultural Management Systems) model, is providing a tool specifically aimed at questions associated with soil, management, and climatic variables in the root zone. The GLEAMS model was successfully tested with the limited data currently available and the model applied to a number of practical questions.

INTRODUCTION

Consistent with the U.S. Department of Agriculture (USDA) mission (U.S.Department of Agriculture, 1989), the authors' goal is to develop and evaluate models sensitive to management and other variables to provide a basis for decision aids in selecting environmentally safe agricultural practices. The GLEAMS (Groundwater Loading Effects of Agricultural Management Systems) model (Leonard and others, 1987) was developed for comparative analysis of complex pesticide, soil, climate, and management scenarios as an extension of an earlier USDA model, CREAMS (Chemicals, Runoff, Erosion, from Agricultural Management Systems) (Knisel, 1980). Because GLEAMS is to be sensitive to specific management effects, its boundaries for comparison are the field edge and the bottom of the plant root zone. Therefore, the model is not a water-quality or ground-water model as such, but a model that provides "loading" functions to and within the larger hydrologic system. Opportunities are provided for coupling of GLEAMS to vadose zone or outputs of larger scale models.

This paper provides examples of GLEAMS model applications at a Plains, Ga., field site--the site of joint USDA-Agricultural Research Service, U.S. Geological Survey, U.S. Environmental Protection Agency, and University of Georgia research (fig. 1). Because the data bases are incomplete at this time, results presented are preliminary and are not meant to represent final conclusions or model validation. Three questions are addressed: (1) How well does GLEAMS simulate system behavior? (2) How do the results obtained during 1989 compare with those expected based on long-term climatic records? (3) How would pesticide masses lost below the root zone under an alternative production system compare to those under the present corn-production system?

MODEL OVERVIEW AND DESCRIPTION

GLEAMS consists of three major components: hydrology, erosion/sediment yield, and pesticide transport. The hydrology component uses daily climatic data to calculate the water balance in the root zone. Input precipitation is partitioned on a daily basis into surface runoff, infiltration, soil storage, evapotranspiration, and percolation below the root zone. The erosion component computes storm-by-storm rill and interrill erosion and sediment yield at the field boundary. The pesticide component simulates up to 10 pesticides in surface runoff, attached to sediment, and in percolate, and the redistribution of pesticides in the root zone each day. Daily, monthly, or annual outputs can be generated in a single run for periods of up to 50 years. Detailed descriptions of model concepts, validation, and limitations are given by Leonard and others (1987); Leonard, Knisel, Davis, and Johnson (1990); and Leonard, Knisel, and Davis (1990).

PROCEDURES AND ASSUMPTIONS

The study site receiving chemical treatment is a rectangular plot about 0.8 ha (hectare) in size; the soil is Eustis loamy sand (sandy, siliceous thermic Psammentic Paleudult). Corn (Zea Maize L.) was planted on June 13, 1989 (Julian date 164), and the plot treated with atrazine, alachlor, carbofuran, and a bromide tracer. Planting date of June 13 was about 70 days later than normal for southern Georgia but was necessary to allow time for installation of monitor wells and other instrumentation. For the simulation, physical data obtained from analyses of soil samples removed from a nearby pit were used inasmuch as actual plot data on soil properties has yet to be summarized. For 1989, simulations were performed for the entire year, using rainfall and irrigation inputs measured directly by a rain gage in the plot after planting and by another nearby rain gage before planting and installation of the plot rain gages.

Pesticide parameters used for the 1989 and long-term simulations are given in table 1. For atrazine and carbofuran, application rates and soil half-life, $t_{1/2}$, were estimated from the data provided by the Athens, Ga., U.S. Environmental Protection Agency laboratory. Remaining parameters were obtained from various reference sources or estimated on the basis of recommended application rates and methods. Application methods are reflected by the parameters for distribution of the applied pesticide between soil and plant canopy, and the depth of pesticide incorporation. The pesticide constant for adsorption by soil organic matter, K_{oc}, is critical in determining mobility in soil water.

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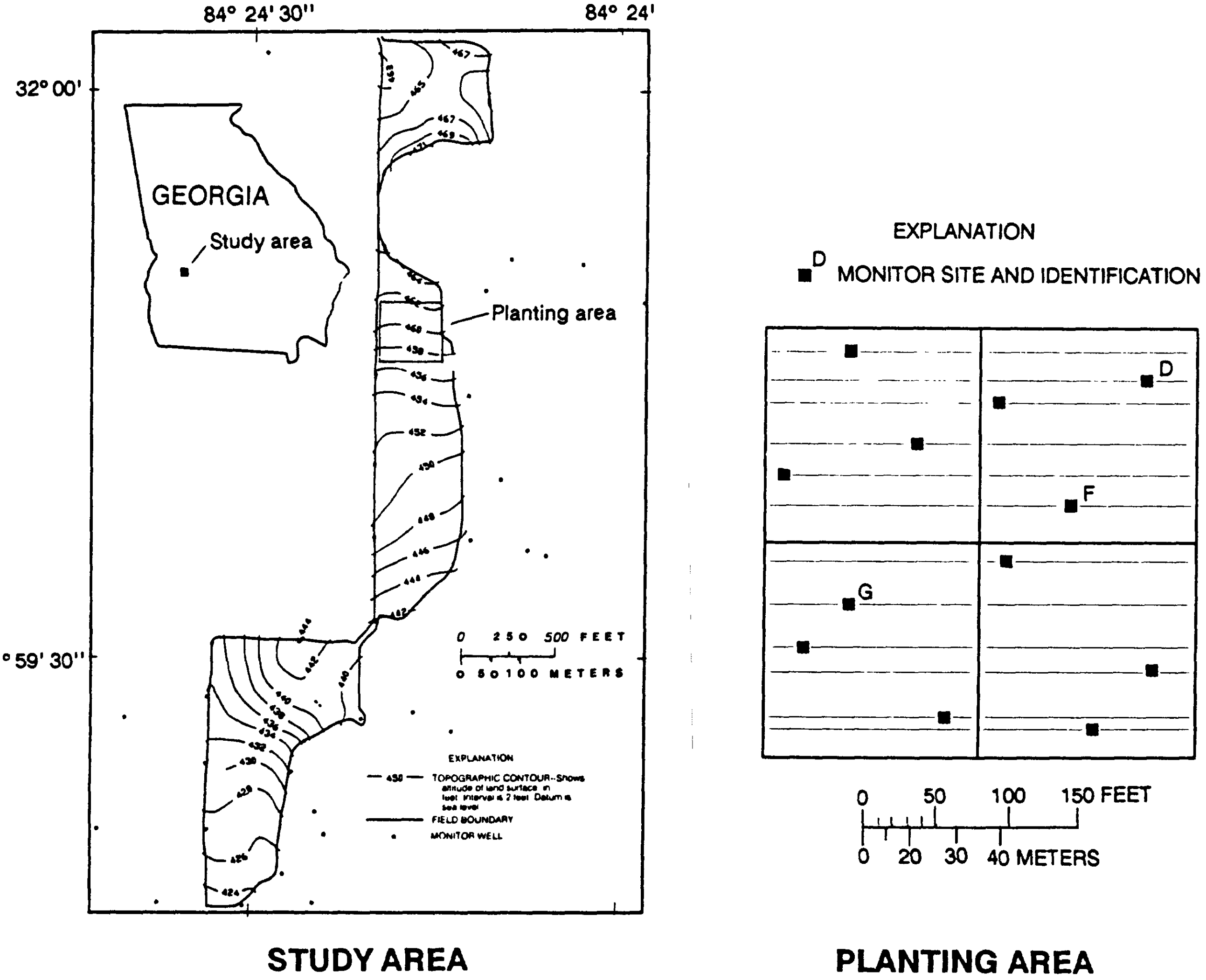
[1] U.S. Department of Agriculture, Agricultural Research Service, Tifton, Ga.


84° 24' 30"
84° 24'
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31° 59' 30"
GEORGIA
Study area
Planting area
0 250 500 FEET
0 50 100 METERS
EXPLANATION
TOPOGRAPHIC CONTOUR--Shows altitude of land surface in feet. Interval is 2 feet. Datum is sea level
FIELD BOUNDARY
MONITOR WELL
EXPLANATION
D MONITOR SITE AND IDENTIFICATION
D
F
G
0 50 100 150 FEET
0 20 30 40 METERS
STUDY AREA
PLANTING AREA

Figure 1. Location of study area, planting area, and monitor sites in the planting area.

Table 1. *Pesticide input parameters for GLEAMS model simulating Plains, Georgia, site*

Pesticide	Application date (Julian)	Application rate (kilograms per hectare)	Fractional distribution		Incorporation depth (millimeters)	Half-life, $t_{1/2}$ days		Foliar washoff fraction	K_{oc}	Solubility (milligrams per liter)
			On soil	On plant		Soil	Foliar			
				1989 plot simulation						
Atrazine	164	1.9	1.0	0	10	14	-	-	100	33
Carbofuran	164	2.0	1.0	0	10	27	-	-	20	351
				50-year plot simulations (1936-85)						
Atrazine	91	1.9	1.0	0	10	14	-	-	100	33
Carbofuran	91	2.0	1.0	0	10	27	-	-	20	351
				50-year alternate management simulations (1936-85)						
Atrazine	91	0.5	1.0	0	10	14	-	-	100	33
Terbufos	91	2.0	1.0	0	50	5	-	-	3,000	5
Sulfonylurea	112	0.05	0.9	0.1	10	50	2	0.8	50	1,200
Pendimethalin	126	1.0	0.9	0.1	50	90	10	0.2	24,000	0.28

RESULTS AND DISCUSSION

Comparisons of observed and simulated concentrations of atrazine and carbofuran with depth in the soil profile for four dates after pesticide applications in 1989 are given in table 2. Results of the simulations are preliminary. However, by visual comparison, simulation results seem to "reasonably" represent field behavior of the two pesticides. Linear regression was used to compare simulated with observed data; the R^2 was 0.87. Certainly, differences between observed and simulated do exist, but because of uncertainties in actual soil properties within the plot, uncertainties in pesticide $t_{1/2}$ with depth and in other model parameters, discussion is not warranted at this stage.

Table 2. *Comparison of simulated and observed[1] pesticide concentrations in Eustis soil profile (0-72 centimeters) on selected days after pesticide application, 1989*

Depth interval in centimeters	Observed, in micrograms per kilogram Days after application				Simulated, in micrograms per kilogram Days after application			
	2	9	27	49	2	9	27	49
				Atrazine				
0-15	640(60)[2]	155(27)	61(7)	43(15)	573	274	49	9
15-30	122(13)	126(23)	75(17)	10(4)	67	91	35	10
30-45	47(6)	43(8)	13(3)	8(4)	27	59	40	13
45-60	13(2)	25(4)	4(2)	8(5)	35	28	31	12
60-72	12(2)	14(3)	2(1)	6(5)	4	16	23	10
				Carbofuran				
0-15	329(56)	26(5)	1(1)	3(2)	377	110	6	1
15-30	303(48)	96(13)	8(4)	5(3)	164	128	20	4
30-45	99(23)	101(12)	15(5)	11(8)	108	184	49	15
45-60	24(6)	112(19)	16(4)	10(6)	50	110	67	27
60-72	8(3)	97(19)	22(4)	11(5)	28	80	70	33

[1] Data supplied by Environmental Research Laboratory, U.S. Environmental Protection Agency, Athens, Ga.

[2] Standard error of the mean.

Accepting that GLEAMS simulations are "reasonable," results of 1989 soil analyses may be compared with simulation results using a 50-year period of historical climate data (table 3). The 50-year rainfall file is actually for Tifton, Ga., located 145 kilometers southeast of the study site, but similar patterns would be expected for the Plains location. Based on 50-year means and ranges in expected pesticide leaching losses, 1989 was an extreme year--that is, in no other year during the 50-year period were simulated losses as great as those simulated for 1989. For example, only in 3 years--1948, 1961, and 1973--did leaching losses of atrazine exceed 100 g/ha (grams per hectare). These results are not unexpected because rainfall in 1989 for the first few weeks after pesticide application was in excess of long-term means. Also, excess irrigation water was applied in 1989 to ensure pesticide movement and the generation of data for model comparisons.

Mean annual pesticide concentrations in leachate below the 72-cm(centimeter)-deep root zone were computed by dividing the total pesticide mass leached during the year by the total percolation volume (table 3). Although these values are not absolutely meaningful because (1) model simulations should not be interpreted as absolute prediction, (2) pesticides move below the root zone in pulses and not mixed uniformly in the total percolate, and (3) the boundary at the bottom of the root zone is far removed from the saturated zone, these computations provide "ballpark" comparisons with established water-quality criteria.

An alternative management scenario was established assuming acceptable pest control could be obtained with a banded application of atrazine over the row--a nematicide/insecticide (terbufos) with much lower mobility and $t_{1/2}$ than carbofuran, and postemergence, over-the-top applications of a sulfonylurea herbicide when the corn was about 30 cm tall followed by an incorporated application of pendimethalin herbicide for residual weed control. An assumed advantage of the sulfonylurea herbicide is that very low rates, about 50 g/ha or less, are required. Pendimethalin has a very large K_{oc} and would not be expected to move in soil water. Simulation results (table 3) demonstrate the reduction in ground-water loadings potentially achievable by change in management. Atrazine losses were reduced in direct proportion to reduction in application rates. Sulfonylurea is moderately mobile because of the K_{oc} and $t_{1/2}$ assumed. Whether the lower concentrations achieved in leachate as a result of lower application rates alleviate potential water quality problems depends on the herbicide's toxicity and its ultimate fate below the root zone.

SUMMARY AND CONCLUSIONS

Three questions were posed as a basis for this paper, and were successfully addressed by model simulations. On the basis of limited comparisons with actual data, the GLEAMS model appeared to provide a "reasonable" representation. Long-term simulations showed that results

Table 3. *Annual summaries of GLEAMS model simulations on Eustis site, Plains, Georgia*

Pesticide	Mass leached below 72 centimeters Root zone, grams per hectare		Concentration in leachate, in micrograms per liter	
	Annual mean	Range for simulation period	Mean annual	Range for simulation period
		1989 plot simulation		
Atrazine	160	-	23.7	-
Carbofuran	899	-	133	-
		50-year plot simulations (1936-85)		
Atrazine	16.5	0 -132	4.7	0 - 30.4
Carbofuran	134	0 -695	38.5	0 -163
		50-year alternate management simulations (1936-85)		
Atrazine	4.3	0 - 34.8	1.2	0 - 8.1
Terbufos	<0.001	0 - <0.001	<0.001	0 - <0.001
Sulfonylurea	1.6	0 - 9.8	0.46	0 - 2.0
Pendimethalin	0	0	0	0

of 1989 should be interpreted as "extreme" because of weather patterns and excess irrigation applied. It was shown that alternate systems may be designed to reduced pesticide transport to ground water.

Changing to pesticides that are less mobile in water reduces leaching losses, but may increase surface runoff losses. We also simulated these losses which should be considered in a management analysis, but space prevents these discussions.

GLEAMS model simulations did not address ground water quality as such. Long-term simulations showed that only in infrequent years (1948, 1961, and 1973) did seemingly large pulses of pesticides move below the root zone. Environmental consequences of these pulses can only be known after transport rates and processes below the root zone are understood and represented in other models.

ACKNOWLEDGMENTS

The authors acknowledge the full participation and excellent cooperation of many individuals in the Environmental Research Laboratory, USEPA, Athens, Ga., and the U.S. Geological Survey, Doraville, Ga.

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PRELIMINARY RESULTS OF A PESTICIDE LEACHING STUDY AT PLAINS, GEORGIA

By Charles N. Smith[1] *and* Rudolph S. Parrish[2]

ABSTRACT

A comprehensive field data base is being developed for testing various chemical-transport models of pesticide leaching. Three Federal agencies (U.S. Environmental Protection Agency, U.S. Department of Agriculture and the U.S. Geological Survey) and the University of Georgia Agricultural Experiment Station established a joint research team to investigate and model pesticide movement in a conventionally tilled corn field in the coastal plain of Georgia. The experimental study design, the monitoring procedures for unsaturated and saturated soil zones, and the data collection methods are presented in the context of a quantitative statistical model testing strategy. Compounds under study include carbofuran (2,3 dihydro-2,2-dimethyl-7-bezofuranyl methylcarbamate), atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5 triazine), alachlor (2-chloro-2'6'-diethyl-N-(methoxymethyl)-acetanilide), and a bromide tracer. Initial application losses were on the order of 15 to 39 percent. Of the three pesticides, only carbofuran persisted for 4 months and moved to levels as deep as 3 meters. Half-lives were estimated for all compounds on the basis of total mass in the soil profile.

INTRODUCTION

Several models that simulate transport and transformation of pesticides in the environment have been developed; these include RUSTIC (Dean and others, 1989), GLEAMS (Leonard and others, 1987), AGG (Fong and Mulkey, 1990), and LEACHM (Wagenet and Hutson, 1989). Rigorous testing of model predictive capability requires that model predictions be compared statistically with field observations (Parrish and Smith, 1990). In addition, field data are necessary for evaluating factors that affect the leaching process. To these ends, a field study to provide a data base for model testing was initiated in 1988 at a site near Plains, Ga. The study site (fig. 1) is in the Fall Line Hills district of the Coastal Plain physiographic province. The Claiborne aquifer recharge area is located in this district.

The U. S. Environmental Protection Agency (USEPA), the U.S. Department of Agriculture (USDA), the U.S. Geological Survey (USGS), and the University of Georgia Agricultural Experiment Station developed a joint research effort to investigate and to model pesticide movement at the Plains site. The study was planned for 5 years duration, beginning with the 1989 cropping season. As early as 1986, the USDA and USGS were involved in characterization studies at this site. The participants are sharing technical expertise and resources to develop a better understanding of physical, chemical, and biological processes that affect leaching, to evaluate spatial and temporal variability, and to develop and test linked models for chemical transport and transformation. One product of this cooperative research effort will be a comprehensive data base that should be useful for testing such models. One interest of USEPA is in testing the predictive capability of RUSTIC, an effort that is currently in progress. The study design is amenable to implementing the testing methodology proposed by Parrish and Smith (1990), as well as other techniques.

This paper describes the field design and presents preliminary results obtained for the first year (the 1989 cropping season).

MATERIALS AND METHODS

Experiment Design

The field site is a 0.81-hectare rectangular area of approximately 91 m (meters) x 91 m, which provides 100 rows of corn when spaced at 0.91 m on centers. For design purposes, the plot was subdivided into four equal-sized quadrants (fig. 2). The site had a slope of less than 1 percent (estimated). Surface runoff occurs toward the south-western corner of the plot. Soil at the site was classified as Eustis by the USDA Soil Conservation Service and is a well-drained sand of hydrologic group A (Asmussen and Smith, 1991).

Conventional agricultural management practices were used for tillage, fertilization, planting, and chemical application. Three pesticides and a bromide tracer were applied in 1989 and were monitored for their downward movement. Chemical applications were monitored directly and soil core samples were collected at various times after application, as described below. A center-pivot irrigation system was installed on the site, supplied from a deep well located approximately 300 m west of the site. The general direction of ground-water flow is from north to south. Irrigation water was applied to the site after chemical application and planting and, also, as required during the growing season to supplement natural rainfall.

During 1988, wells and soil-solution samplers (suction lysimeters) were installed at various locations within the site on crop row centers for the purpose of monitoring concentrations of pesticides and bromide. As shown in fig. 2, 12 permanent monitoring sites were located randomly (3 per quadrant). Each of these consisted of three 5-cm (centimeter)-diameter wells screened individually at three depth increments corresponding to the top, middle, and lower zones of the Claiborne aquifer, and one 5-cm fully penetrating well. Also, at 8 of the 12 sites, 7 soil-solution samplers were installed at depths ranging from 0.6 m to 4.3 m in 0.6-m increments. These samplers were used to provide information on maximum depths of leaching. Concentrations derived from soil-core samples are used to evaluate model performance.

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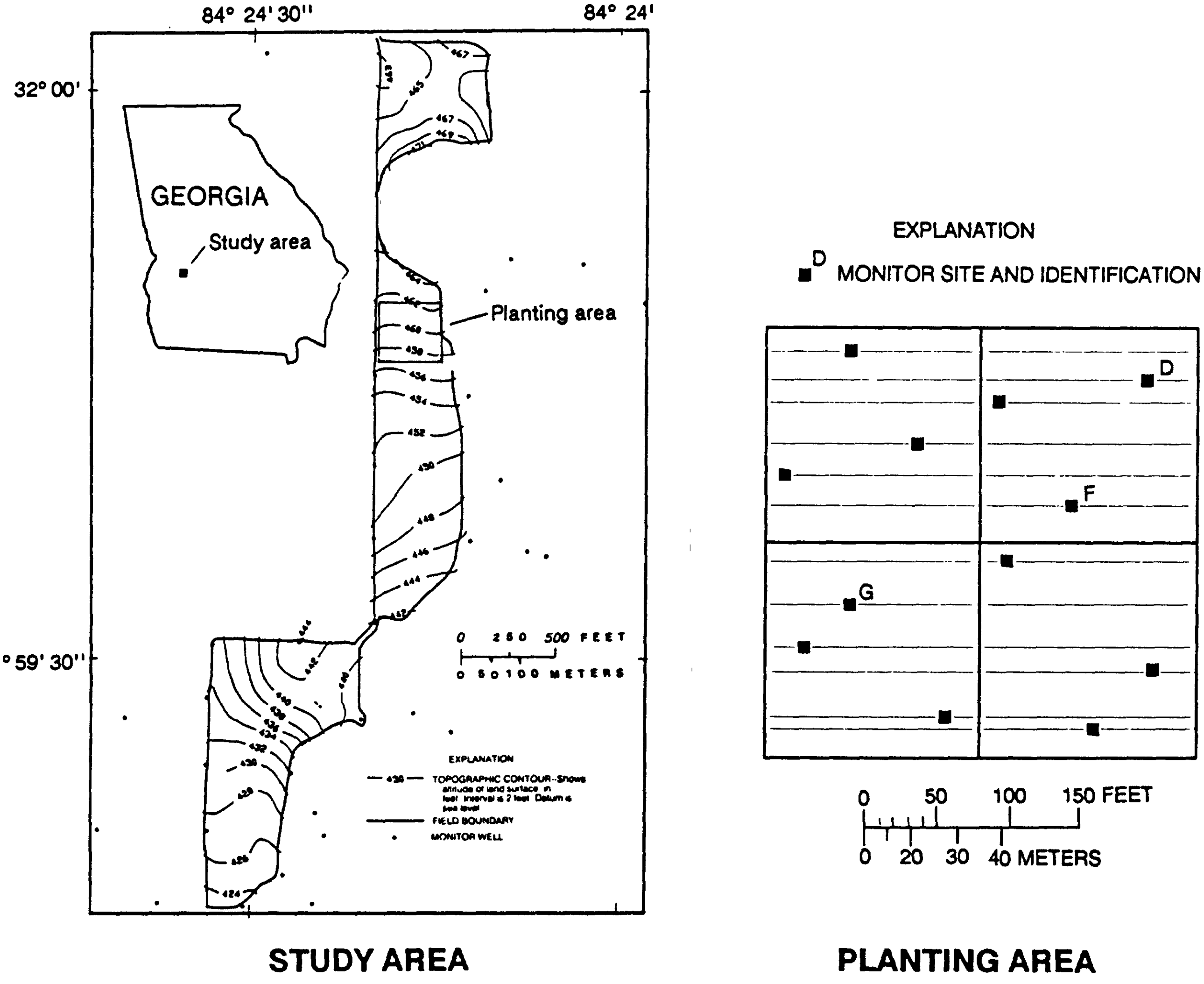
[1] U.S. Environmental Protection Agency, Athens, Ga.
[2] Computer Sciences Corporation, Athens, Ga.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84° 24'
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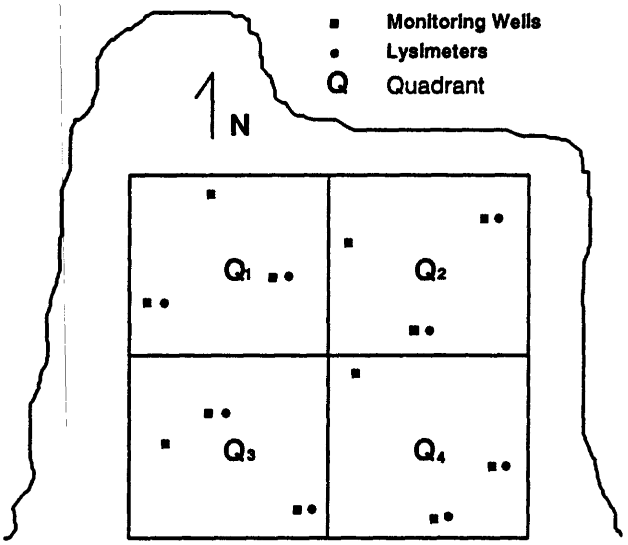
GEORGIA
Study area
Planting area
0 250 500 FEET
0 50 100 METERS
EXPLANATION
438 TOPOGRAPHIC CONTOUR--Shows altitude of land surface in feet. Interval is 2 feet. Datum is sea level
FIELD BOUNDARY
MONITOR WELL
EXPLANATION
D MONITOR SITE AND IDENTIFICATION
D
F
G
0 50 100 150 FEET
0 20 30 40 METERS
STUDY AREA
PLANTING AREA

Figure 1. Location of study area, planting area, and monitoring sites in the planting area.

Chemical Applications

Liquid forms of atrazine, carbofuran, and alachlor were applied individually at label-recommended rates immediately following planting. Potassium bromide salt, in liquid form, was applied as a conservative tracer following the pesticide application. A conventional tractor-mounted spray rig was used, having six number 8003 nozzles on 30-cm centers,which provided lateral coverage of 1.8 m (across two crop rows). With the exception of carbofuran, actual application rates were monitored by the use of filter disks located randomly within the field, as described in Smith and others (1985). The filter disks were positioned so as to intercept the pesticide spray; they were collected immediately after being sprayed and were shipped to a laboratory for analysis. Target rates for atrazine, alachlor, carbofuran, and bromide were, respectively, 2.24, 2.8, 2.24, and 112 kg/ha^{-1} (kilograms per hectare). The carbofuran application rate was not monitored with filter disks because of the risk of worker exposure to this compound during postapplication collection.

Immediately following the chemical applications, 1.3 cm of irrigation water was applied. This induced movement of the compounds below the immediate surface layer.


■ Monitoring Wells
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Q Quadrant
N
Q1
Q2
Q3
Q4

Figure 2. Field monitoring sites, Plains, Georgia, 1989.

Soil-Core Sampling

Analysis of background soil samples collected prior to initiation of the study did not reveal any traces of the test compounds. On each of several dates after application, soil cores were obtained from various depths (depending on the anticipated depth of leaching) at 12 to 20 random locations on row centers within the field. Soil samples were obtained from as many as 27 depths ranging to 9.1 m, spaced as follows: every 0.15 m down to a depth of 1.8 m, every 0.3 m down to 4.6 m, and every 0.8 m down to 9.1 m. Hand augers were used to collect samples down to 3 m during the growing season (Smith and others, 1985), and a drill rig equipped with a continuous-coring device (CME hollow-stem split-tube bearing-head sampler with 15-cm liners) was used to collect soil cores from deeper zones prior to application and after harvest. The timing of the sampling events was determined on the basis of rainfall quantity and expected degradation rates. For 1989, samples were collected at 2, 9, 27, 49, 91, and 119 days after application.

Meteorological Data

Precipitation data were recorded at 5-minute intervals at four local sites. Pan evaporation, windspeed, wind direction, ambient air temperature, and rainfall (long-term) data were collected at a site adjacent to the plot and also at the University of Georgia Plains Experiment Station located 5 kilometers from the site.

Runoff

A soil berm was constructed around the perimeter of the plot to control runoff. An H-flume (0.46-m width) was installed at the southwest corner of the plot to measure sediment and chemical transport in runoff. A stage recorder and an automated stage-activated runoff-sample collector were installed (Smith and others, 1990).

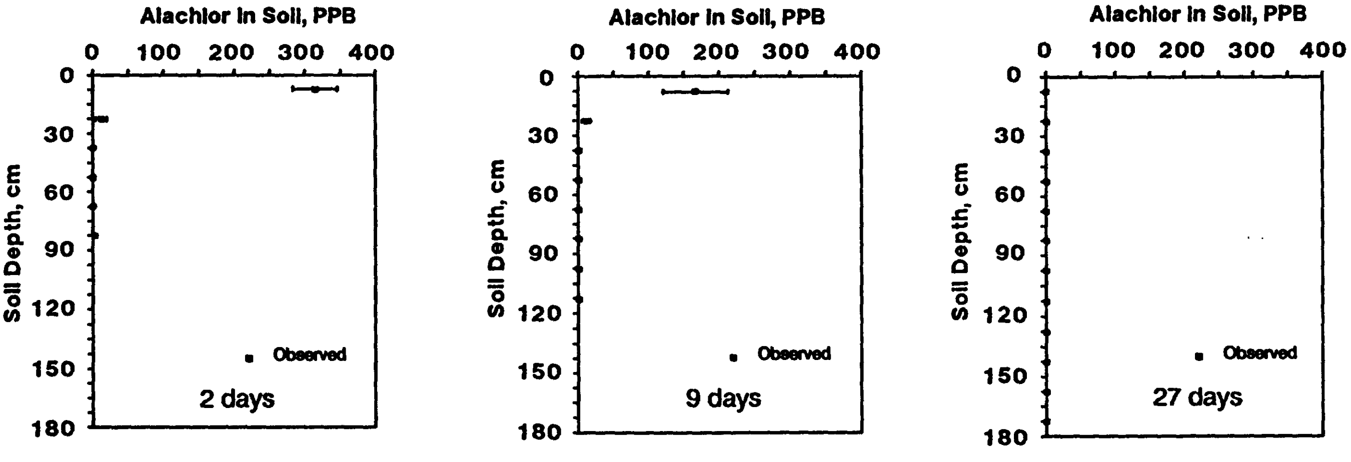
RESULTS AND DISCUSSION

Application Rates

Application rates for atrazine and alachlor, as measured by filter disks, differed from calculations based on the actual total mass of compounds applied to the field. Measured application rates for atrazine and alachlor were, respectively, 1.90±0.023 and 1.70±0.018 kg/ha^{-1}, based on sample sizes of 87 and 100. The differences amounted to a 15 percent loss for atrazine and 39 percent for alachlor. It is believed that the losses from the separate applications are due jointly to drift and volatilization. Results for bromide are not yet available. In a previous study (C.N. Smith and R.S. Parrish, U.S. Environmental Protection Agency, written commun., 1991), metolachlor [2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl) acetamide] applied in a similar manner exhibited losses on the order of 26 percent.

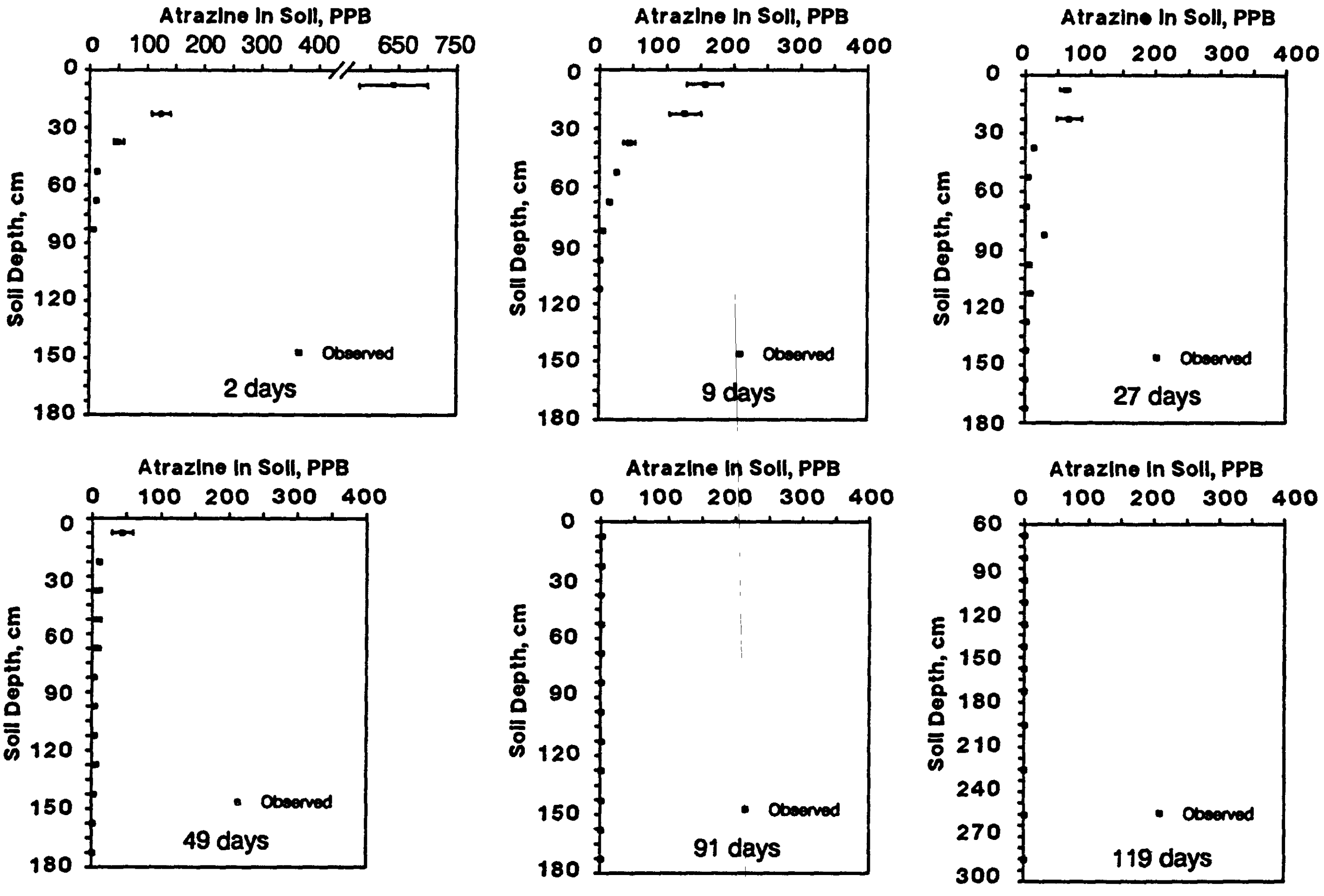
Postapplication Monitoring

All compounds were monitored on 2, 9, 27, 49, 91, and 119 days after application. On sampling days 2 through 91, soil cores were obtained at 20 randomly located sites; on day 119, 20 sites were sampled down to a depth of 1.5 m, and at 12 of those sites, samples were obtained down to 9.1 m. Figures 3, 4, and 5 show concentration profiles for alachlor, atrazine, and carbofuran, respectively. For alachlor maximum depth of pesticide movement was to the 15- to 30-cm depth increment, and very little measurable residue remained on day 27. Atrazine was more persistent and moved deeper than alachlor. After 2 days, atrazine was detected at the 76- to 91-cm depth increment, with a maximum leaching depth observed on day 49 of 152 to 168 cm. The profile has a general J-shaped appearance except for day 27 where a peak is observed at the 15-to 30-cm depth. The carbofuran profile had a similar J-shape on day 2 but quickly



* Bar = Standard deviation of observed mean

Figure 3. Alachlor in soil profile over sampling period ,Plains, Georgia, site, 1989.



* Bar = Standard deviation of observed mean

Figure 4. Atrazine in soil profile over sampling period, Plains, Georgia, site, 1989.

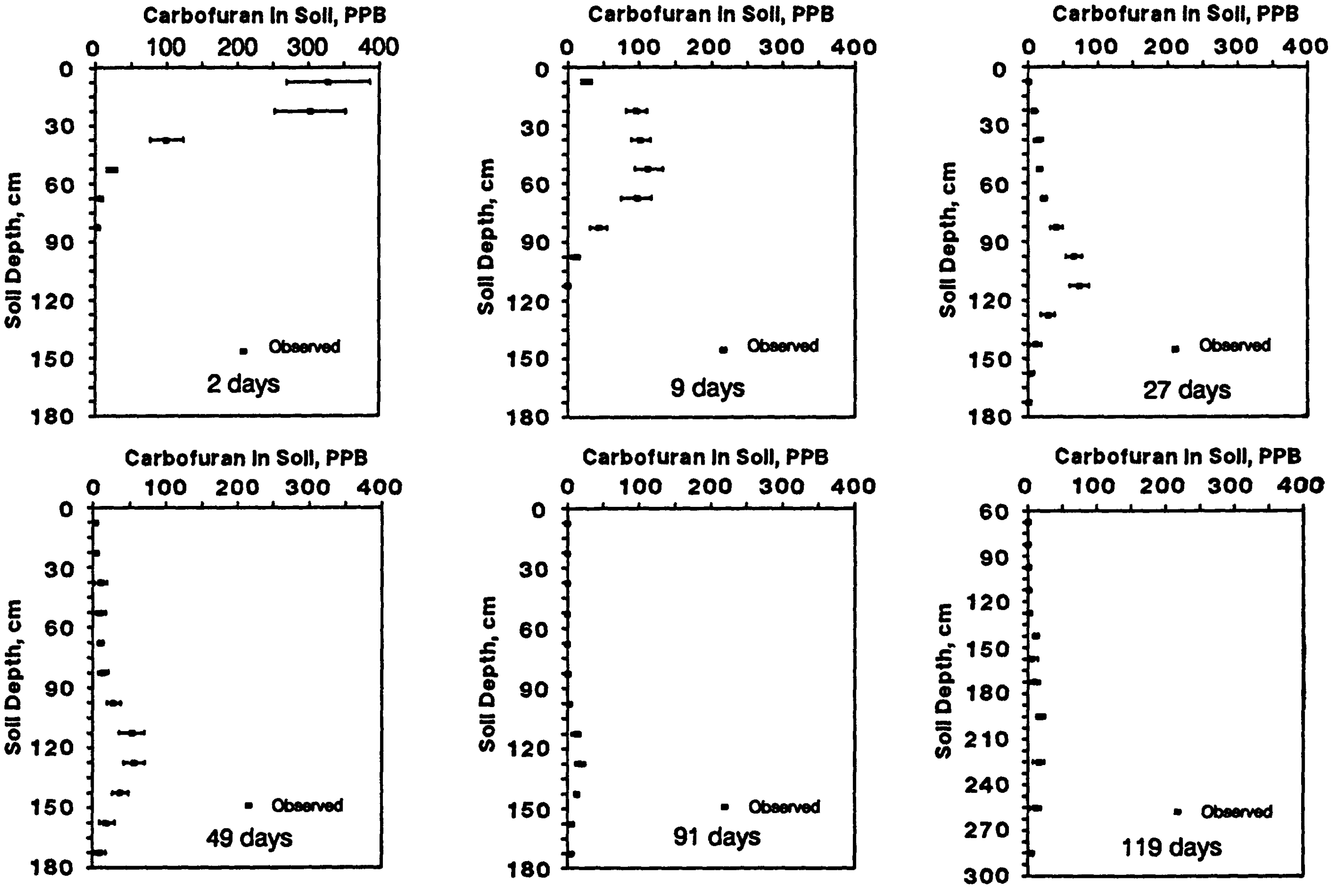
developed a definitive peak that appeared to move downward progressively. On day 119, carbofuran was observed in low concentrations at 3 m. This was the only pesticide that persisted at measurable levels for the entire sampling period.

Field Transformation Rates

Transformation rates with depth are difficult to measure in the field because pesticide transport and transformation occur simultaneously. By combining measurements at all depths at different times after application, the total mass of a compound that remains in the soil column can be estimated (figs. 3, 4, and 5). These values can be used to derive a profile-averaged half-life. For atrazine, the observed half-life was 14.2 days; for alachlor, it was 2.6 days; and for carbofuran, it was 26.5 days. Previous studies (Rao and others, 1986; Smith and others, 1990) have revealed that transformation rates decrease with increasing depth for the compounds metolachlor and aldicarb [2-methyl-2-(methylthio) propionaldehyde O-(methylcarbamoyl) oxime]. A profile-averaged half-life measures a rate that actually varies within the soil profile, and it is believed that rates are higher in the upper soil zones.

RUSTIC Testing

The data base being developed for the Plains, Ga., site can be used to test a variety of models, including RUSTIC (Dean and others, 1989) which includes linked components corresponding to the root zone, the vadose zone, and the saturated zone. A primary objective for USEPA-Athens staff is to test the predictive capability of RUSTIC -- a project that currently is in progress. Initial testing will include comparisons between observed and predicted results for the three pesticides for the 1989 cropping season. Results will be evaluated using the quantitative-testing methodology proposed by Parrish and Smith (1990). Input parameter sets for RUSTIC are being derived from several sources, including site-specific data, the RUSTIC user manual, and the DBAPE Data Base Analyzer and Parameter Estimator (DBAPE) soils data base (Imhoff and others, 1990).



* Bar = Standard deviation of observed mean

Figure 5. Carbofuran in soil profile over sampling period, Plains, Georgia, site, 1989.

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OVERVIEW OF RESEARCH ON CONTAMINATION OF THE SUBSURFACE BY CRUDE OIL AT THE BEMIDJI, MINNESOTA, TOXIC SUBSTANCES RESEARCH SITE

By Marc F. Hult[1]

ABSTRACT

The U.S. Geological Survey Toxic Waste Hydrology Program began an interdisciplinary research project in 1983 at the site of a crude-oil spill near Bemidji, Minnesota. The spill occurred in 1979 when a pipeline transporting crude oil broke. After cleanup efforts were completed in 1980, about 400,000 liters of oil remained in the unsaturated zone and near the water table. This continues to be a source of contaminants to a shallow outwash aquifer. The oil is moving as a separate fluid phase, as dissolved petroleum constituents in ground water, and as vapors in the unsaturated zone. Native microbes are converting the petroleum derivatives into carbon dioxide, methane, and other biodegradation products. The objective of the project is to improve an understanding of the mobilization, transport, and fate of crude oil in the shallow subsurface. Research is conducted within four broad disciplines by scientists from the U.S. Geological Survey and from several academic institutions. Currently, 20 research projects are active. This paper provides a general description of the site and describes project objectives, history, and organization.

INTRODUCTION

The U.S. Geological Survey (USGS) began an interdisciplinary research project in 1983 to study the mobilization, transport, and fate of crude oil in the shallow subsurface. This paper provides a general description of the site and project objectives, history, and organization.

DESCRIPTION OF SITE

On August 20, 1979, the subsurface was contaminated near Bemidji, Minn. (fig. 1), when a pipeline burst, spilling crude oil onto a glacial outwash aquifer. After cleanup efforts were completed, approximately 400,000 liters of crude oil remained (Hult, 1984).

The spill occurred in the recharge area of a local flow system that discharges to a small lake 350 m (meters) down the hydrologic gradient from the pipeline. The land surface is formed by pitted and dissected glacial outwash of regional extent that is 5 to 10 m thick. The outwash is underlain by other stratified glacial deposits that differ considerably in texture and origin, and, at a depth of about 20 m, consist of a regionally persistent and uniform till.

The spilled crude oil infiltrated the ground and some percolated to the water table. A large area sprayed by the leaking oil (referred to as the "spray zone"), contains oil only in the upper 1 m. Oil is present near the water table about 1 to 8 m below land surface. Soluble petroleum compounds and intermediate degradation products have dissolved in and are moving with ground water. Volatile constituents are diffusing through the unsaturated zone as vapors.

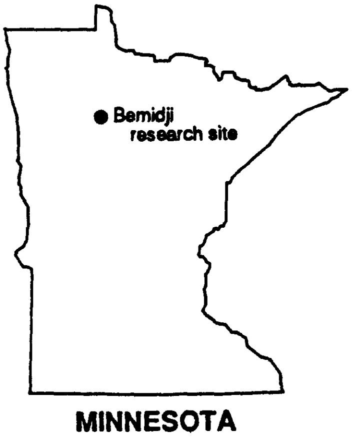

Figure 1. Location of Bemidji research site, Minnesota.

In the 11 years since the spill, petroleum has moved about 30 m down the hydrologic gradient as a separate fluid phase, constituents dissolved in ground water have moved at least 200 m, and vapors in the unsaturated zone have moved horizontally about 100 m. The petroleum source is becoming increasingly more viscous, dense, and depleted in volatile compounds because of selective dissolution and volatization. Some of the petroleum derivatives moving with ground water and through the unsaturated zone are being biodegraded to carbon dioxide, water, methane, and other biodegradation products. The volume of ground water that has become anoxic continues to expand.

RESEARCH OBJECTIVES AND HISTORY

The overall research objectives are to improve understanding of the mobilization, transport, and fate of crude oil in the shallow subsurface; and to develop predictive models for use as tools in understanding the transport and fate of contaminants. Previous results of the research have been summarized in Hult (1984), Franks (1987), Ragone, (1988), and Mallard and Ragone (1989).

The emphasis during the first years of the project has been on characterization of the hydrogeochemical environment, identification of the controlling geochemical reactions, and preliminary assessment of process critical to the development of realistic simulations. Several preliminary ground-water flow, solute transport, and multiphase models were constructed.

During the next 5 years, the emphasis will be on mass-balance approaches to describe and predict quantitatively

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(1) the movement and changes in composition of the crude oil, and (2) the geochemical and microbiological processes in the saturated and unsaturated zones. Progress is expected toward the goal of developing models of the system that provide tools with which to examine major environmental processes and that have transfer value to other hydrologic and geochemical environments.

Little information concerning the hydrogeology and natural geochemistry of the site was available at the time of the pipeline break, but the nature and extent of contaminant introduction were well known because initial remedial measures were prompt. A major, early effort of the research project was a description of the site specific hydrogeologic framework and development of field facilities needed for the proposed investigations.

During 1979 and 1980, and since 1983, water and oil levels have been monitored in selected wells. Beginning in 1984, a coordinated, synchronous sampling of wells along a transect through the contaminated zone has been conducted annually.

The site has proven to be well suited for the intended research, but some characteristics are more complex than originally anticipated. Original assumptions that proved valid include the following:

(1) Evolution of the plume has been relatively unaffected by additional human activities, although some tree planting and fertilization has occurred since the end of remedial action in 1980.

(2) Because the site is remote, the spill has had no effect on supplies of drinking water, and no other significant sources of contaminants or manmade hydraulic stresses have been identified. Processes observed result from the response of the natural system to the spill.

(3) The contaminant source was a single, virtually homogeneous fluid. Significant compositional variations now present within the oil bodies appear to be caused by differential removal of soluble and volatile compounds by dissolution and vaporization.

(4) The contaminant plume consists in a continuum of compounds that range from very mobile and readily biodegradable to very immobile and recalcitrant. The presence of homologous series of compounds with systematically and widely variable properties permits extrapolation of the predicted transport and fate of many compounds on the basis of detailed understanding of the transport and fate of representative compounds.

(5) The oil phase has migrated only a short distance compared to the plume of dissolved constituents, but the surface area of the oil body in contact with water and, therefore, the potential area for dissolution has increased with time.

Some factors, however, have required modification of the planned approach:

(1) The distribution of contaminants in the unsaturated zone is very important to mobilization and fate of a substantial part of the total carbon flux. Some oil remains perched in the unsaturated zone above the water table but several meters below land surface. The effect of these perched bodies on recharge and water quality is poorly known. Highly weathered oil residues are present in the upper meter of the unsaturated zone over a large area, particularly in the area referred to as the "spray zone." This source has created a plume of contaminants chemically distinct from, and in places superposed on, the plume created by dissolution of oil at and below the water table. The weathered oil inhibits infiltration of precipitation and presumably affects the distribution of recharge to the saturated zone.

(2) Construction of sampling points at closely spaced vertical intervals has proved difficult in some important parts of the system because the water table is locally too deep to allow pumping of multilevel samplers with suction or peristaltic pumps. Closely spaced sampling points are required because of steep geochemical and biochemical gradients within the plume.

(3) Heterogeneities in sediment texture cause significant local variations in vertical and horizontal flow both in the unsaturated and saturated zones. In particular, fine-grained zones have caused the ground-water plume to spread more slowly than originally anticipated, perching of the oil in the unsaturated zone, and localization of the vertical migration of vapors through the unsaturated zone.

ORGANIZATION OF RESEARCH

Coordinated efforts by researchers in the National Research Program (NRP) and Districts of the Water Resources Division (WRD) and Geologic Division (GD) of the USGS, and several academic institutions have contributed to the scientific effort. Currently, 20 projects in 4 major research disciplines are active at the site.

Four major research disciplines were identified during development of a long-term plan for the site: hydrogeology, multiphase transport, geochemistry, and microbiology. Multiphase transport encompasses research on characterization of the source term (oil-water and oil-air interactions), movement of the oil body, and processes in the unsaturated zone. The unsaturated zone research includes the movement of vapors and their biologically mediated transformations, interaction of the vapors with soil moisture and sediment, and changes in the composition of the oil owing to vaporization and dissolution by ground water.

A summary of objectives, accomplishments, plans, and needs for each of four major research disciplines was prepared in collaboration with the principal researchers involved in each discipline. One purpose of these summaries is to show how different project elements interact. An unintended effect of the groupings is to deemphasize interactions between research elements in different research disciplines. Moreover, some project elements have major emphasis in more than one discipline.

Hydrogeology

The principal objective is to describe the hydrogeology of the site in sufficient detail and with sufficient certainty to allow quantitative modeling of major hydrologic, geochemical, and biologic processes. Most hydrogeologic investigations at the site are conducted primarily for the purpose of defining the local ground water-flow field as needed for the overall project, rather than with the intention of testing research hypothesis with broad transfer value. Consequently, although the hydrogeologic investigations are very important to the success of the project, they are not considered a major focus of scientific activity. A significant exception to this generalization is development of ground-penetrating radar techniques.

Investigations include:

(1) Geophysical characterization of the subsurface (G.R. Olhoeft, USGS, GD, Denver, Colo.).
(2) Hydrogeologic controls on contaminant transport (M.F. Hult, USGS, WRD, St. Paul, Minn., and P.C. Bennett, University of Texas, Austin).

Multiphase Transport

The source-term investigations are a major thrust of the project. Although research was begun at the laboratory scale, most field-scale investigations have begun within the last 2 years. Overall objectives are to (1) describe and simulate quantitatively the physical movement and distribution of the oil body, (2) quantify oil-to-water and oil-to-air phase transfer (mobilization), and (3) improve understanding of the transport and fate of organic vapors in the unsaturated zone.

Investigations include:

(1) Characterization of flow in air-oil-water systems (H.I. Essaid, USGS, WRD, NRP, Menlo Park, Calif.; W.N. Herkelrath, USGS, WRD, Deer Creek, Calif.; and K.M. Hess, USGS, WRD, Marlborough, Mass.),
(2) Characterization of oil and derivatives by Nuclear Magnetic Resonance (K.A. Thorn, USGS, WRD, NRP, Arvada, Colo.).
(3) Transport processes in the unsaturated zone (M.F. Hult, USGS, WRD, St. Paul, Minn.).
(4) Transport of carbon dioxide in the unsaturated zone (R.W. Healy and R.G. Striegel, USGS, WRD, NRP, Lakewood, Colo.).
(5) Effect of hydrophobic soils on the distribution of recharge (J.L. Nieber, University of Minnesota, Department of Agricultural Engineering, St. Paul).
(6) Changes in oil properties (M.K. Landon, and M.F. Hult, USGS, WRD, St. Paul, Minn.).
(7) Characterization of oil mobilization processes (H.O. Pfannkuch and Li-Feng Guo, University of Minnesota, Department of Geology and Geophysics, Minneapolis).

Geochemistry

The objectives are to understand and describe quantitatively the organic and inorganic geochemical reactions that occur in the aquifer as the components of crude oil interact with the aquifer material and are transported downgradient, and the processes that affect the transport and alteration of hydrophobic constituents by dissolved and colloidal contaminant phases. Salient processes include the effects of redox conditions, organic-inorganic complexion, and partitioning on stationary surfaces.

Investigations include:

(1) Role of organic acids in ground water affected by crude oil (G.R. Aiken, USGS, WRD, NRP, Arvada, Colo.).
(2) Transport mechanisms of hydrophobic organic chemicals (P.D. Capel, USGS, WRD, St. Paul, Minn., and E.T. Furlong, USGS, National Water Quality Laboratory, Arvada, Colo.).
(3) Silicate diagenesis and metal organic interactions (P.C. Bennett, University of Texas, Austin).
(4) Redox geochemistry and *in-situ* hydrocarbon degradation (M.J. Baedecker and I.M. Cozzarelli, WRD, NRP, Reston, Va.).
(5) Pathways for methane production and degradation (Kinga Revez, USGS, WRD, NRP, Reston, Va.).

Microbiology

The objectives are to (1) investigate the rates and processes by which bacteria are capable of degrading organic components under aerobic and anaerobic conditions and, (2) to investigate microbial processes on mineral surfaces and to characterize the microbes that actively weather minerals.

Investigations include:

(1) Anaerobic microbial degradation of crude oil (D.R. Lovley, USGS, WRD, NRP, Reston, Va.).
(2) Geomicrobiology of oil degrading bacteria (Franz Hiebert and P.C. Bennett, University of Texas, Austin).
(3) Degradation and transport of hydrocarbons and microbial community characteristics in aquifer materials (Fu-Hsian Chang, Bemidji State University, Bemidji, Minn.).

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AIR, OIL, AND WATER DISTRIBUTIONS AT A CRUDE-OIL SPILL SITE, BEMIDJI, MINNESOTA

By H.I. Essaid[1], W.N. Herkelrath[1], *and* K.M. Hess[2]

ABSTRACT

As part of a research program aimed at improving our understanding of immiscible-fluid movement in the subsurface, we developed a methodology for determining oil, water, and air saturation distributions in the subsurface. The method was tested at a crude-oil-spill site near Bemidji, Minnesota. Relatively undisturbed sediment cores were collected with a 1.5-meter-long piston core barrel at seven locations along a 120-meter longitudinal transect through the more southerly of the two oil pools. In order to immobilize the fluid phases, the core was rapidly frozen to below -60 degrees Celsius, in an alcohol bath cooled with dry ice, then immediately cut into approximately 7.8-centimeter lengths. The core sections were capped and sealed for laboratory analysis of fluid contents. Oil, water, and air contents of the samples were determined gravimetrically. The oil was extracted using strips of porous polyethylene that absorb oil but not water. The samples were then oven-dried to remove the water. After fluid-saturation analysis, particle-size distributions were determined for each sample.

On the basis of the field data, a clearly defined oil lens floats on the water table. The center of the oil lens has depressed the water table, and the flanks of the lens have migrated within the capillary fringe. There is poor correspondence between thicknesses of oil in wells and the actual distribution of oil in the subsurface. Sediment heterogeneity appears to play an important role in the distribution of the oil phase. The data were used to test a cross-sectional, multiphase flow model. Results of simulations indicate that the observed oil lens cannot be reproduced considering only the uniform mean properties of the sediments. Representations of observed spatial variability were incorporated into the model, illustrating the sensitivity of oil saturation to heterogeneity of sediment properties. The simulated oil lenses reproduce the general features of the observed lens, but do not reproduce the details of the subsurface oil distribution.

INTRODUCTION

Detailed characterization of the subsurface distribution of fluid saturations is needed to understand the transport of immiscible contaminants, and to allow the testing of numerical models that simulate their movement. Direct mapping of subsurface oil distributions could also be used to test geophysical techniques being developed to estimate the distribution of hydrocarbons. Generally, information regarding the presence and movement of an immiscible contaminant, such as oil, is deduced from the thickness of oil that accumulates in wells. However, the relation between oil thicknesses in wells and the distribution of the oil in the adjacent sediment is very complex and poorly understood. As part of a study of immiscible fluid transport in the subsurface, a method was developed and tested for measuring the spatial distribution of oil, water, and air saturations[3]. The method was applied to a crude-oil spill at the U.S. Geological Survey's Toxic Substances Hydrology Program research site near Bemidji, Minn. (fig. 1).

To determine the *in situ* oil, water, and air saturations it was first necessary to develop a field technique to collect relatively undisturbed sediment samples while maintaining the original distribution of pore fluids. The samples were then analyzed in the laboratory using a gravimetric method that employs hydrophobic porous polyethylene (PPE) to extract the oil phase. The data were used to test a numerical multiphase flow model. This paper describes the saturation determination technique, and presents the field data with results of preliminary numerical simulations.

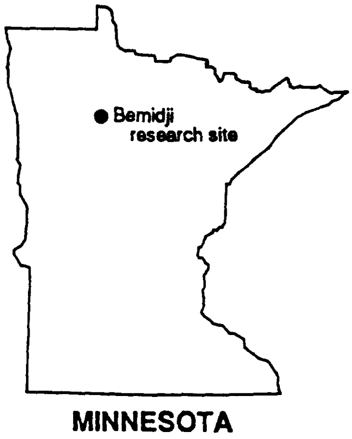

Figure 1. Location of Bemidji research site, Minnesota.

METHODS

The sediments at the site are highly permeable, unconsolidated, stratified-drift and outwash deposits composed of sand and gravel. Because the saturated sand lacks cohesion, traditional split-spoon methods could not be used to recover continuous cores below the water table. Instead, a fixed-piston, wireline core barrel (Zapico and others, 1987) was used to collect 1.5-m (meter)-long, 47-millimeter-diameter cores in clear polycarbonate liners. The piston imposes a suction on the sediments in the core barrel, inhibiting sample and fluid loss during retrieval. Cores were examined immediately; the lithology was described and the presence or absence of oil noted. The cores were then frozen onsite to below -60 °C (degrees Celsius) in an alcohol-dry ice bath. Freezing the core immobilized the fluids so that the core could be cut into sections averaging 7.8 centimeters in length using a circular saw with a masonry blade. The core segments remained frozen long enough to be capped and sealed. The sealed sections were transported to the lab for fluid-saturation analysis. Following coring, four of the boreholes were completed with 1.5-m stainless-steel screens placed to intercept the oil lens.

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[1] U.S. Geological Survey, Menlo Park, Calif.

[2] U.S. Geological Survey, Marlborough, Mass.

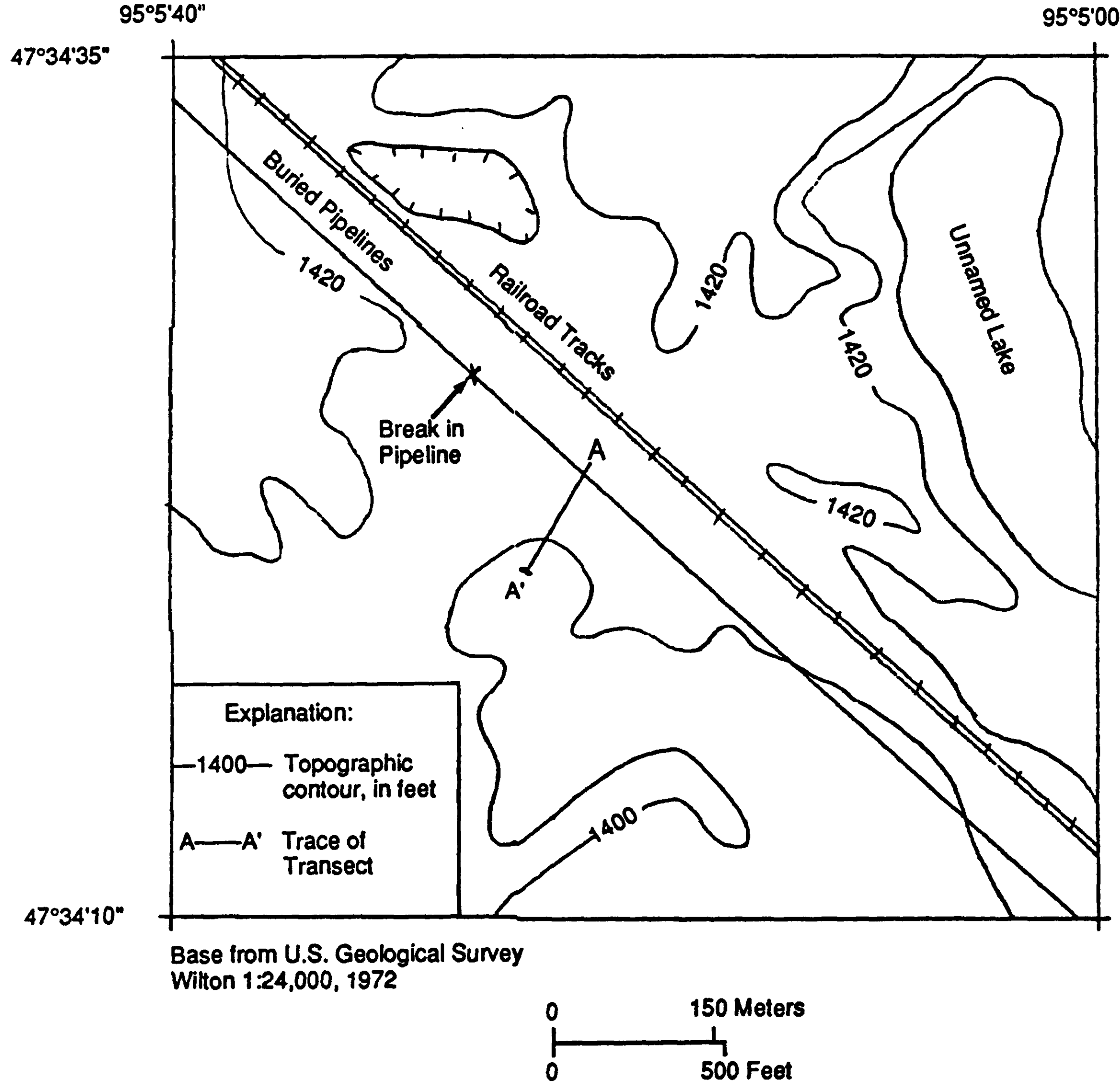
[3] Fluid saturation refers to the degree of saturation of the fluid phase expressed as a fraction of the total pore space.

A method developed by Cary and others (in press) to extract immiscible organic liquids from laboratory samples was modified to accommodate the field samples. The procedure involves gently shaking a slurried sediment into which a preweighed strip of hydrophobic PPE has been placed. The PPE absorbs the oil phase only, so that the oil content of the sample can be determined from the change in mass of the PPE strip. Following extraction of the oil, the sample was oven dried at 105 °C to remove the water. The sample water content was calculated from the initial sample mass minus the mass of oil and dry sediment. Measured fluid and solid densities were used to calculate porosity and water and oil saturations on the basis of the initial sample volume. The remaining volume fraction of pore space was assumed to have been filled with air. Absorption of water and sediment by the PPE, in addition to the oil, can introduce as much as a 4 percent increase in the measured oil mass. An additional ± 5 percent error may be introduced when the mass is converted to saturation because of uncertainties in the porosity calculation and oil density measurement. Following saturation analysis, the particle-size distribution for each sample was determined by standard sieve methods.

RESULTS

Field Data

In October 1989, core samples were collected along a transect through the more southerly oil pool, parallel to an assumed direction of ground-water flow (fig. 2). Cores were collected from 7 boreholes along the transect, yielding 146 samples for fluid saturation determination. Figure 3 is a vertical cross section showing sample locations, oil thicknesses in the previously existing wells, and computer-generated contours of equal oil saturation along the transect. Fluid levels in wells were used to determine the water-table altitude. In wells containing oil, an apparent



Base from U.S. Geological Survey Wilton 1:24,000, 1972

Figure 2. Location map showing transect. (Modified from Hult, 1984, fig. 4.)

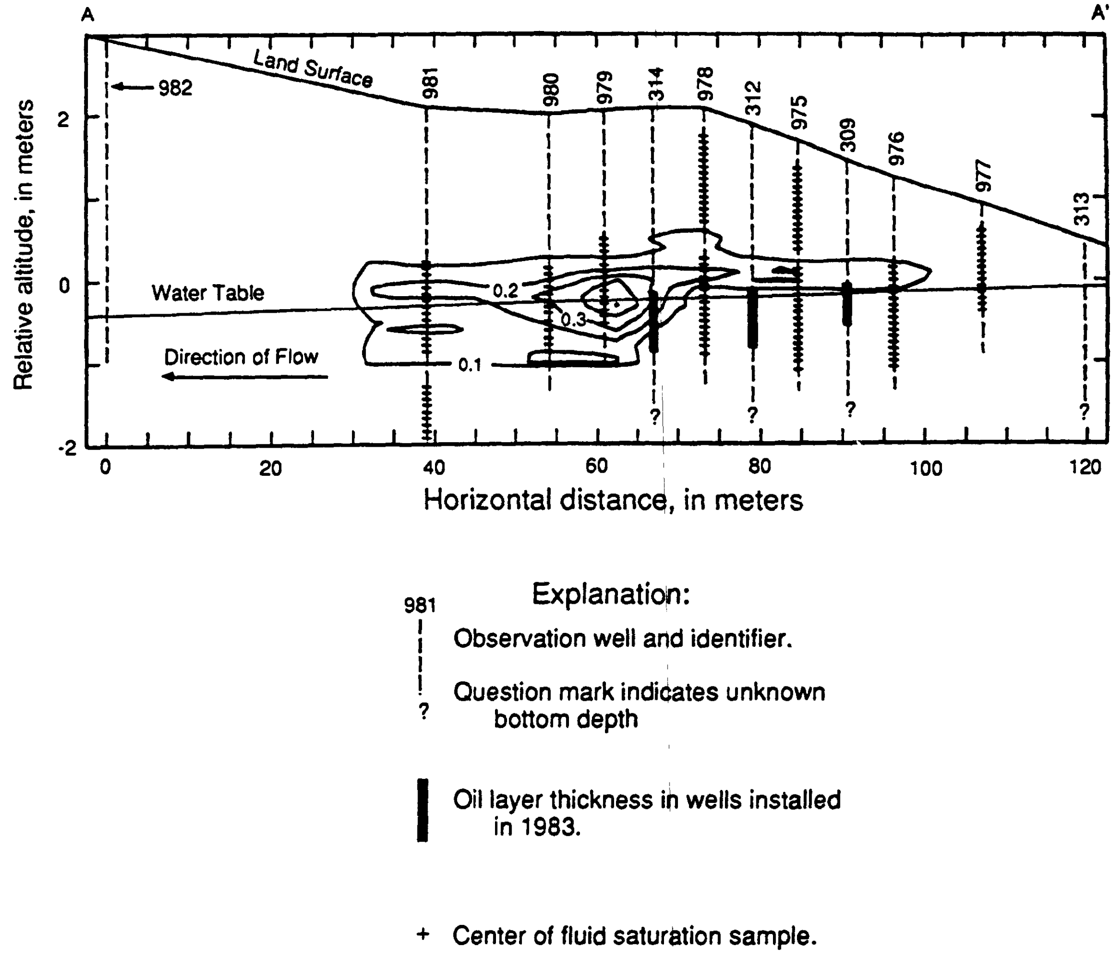

A
A'
Land Surface
982
981
980
979
314
978
312
975
309
976
977
313
Water Table
Direction of Flow
0.2
0.3
0.1
?
Relative altitude, in meters
2
0
-2
0
20
40
60
80
100
120
Horizontal distance, in meters
Explanation:
981
Observation well and identifier.
Question mark indicates unknown bottom depth
Oil layer thickness in wells installed in 1983.
+ Center of fluid saturation sample.

Figure 3. Vertical cross-section showing core samples locations, apparent water table, oil thicknesses in wells, and lines of equal oil saturation (contour interval = 0.1). Altitude is relative to an arbitrary datum.

water table was calculated on the basis of the known oil thickness and density. A clearly defined oil lens floats on the water table. A localized zone of high oil saturations occurs at the center of the lens where one sample has the maximum saturation of 0.6. Below the water table and downgradient from the center of the oil lens, a large area has oil saturations of less than 0.20. The center of the oil lens has significantly displaced water in the saturated zone; however, the leading and trailing edges of the lens appear to have migrated within the capillary fringe. No oil was detected in the borehole farthest downgradient (borehole 982). It is interesting to note the poor correspondence between oil-layer thicknesses in wells and the oil distribution in the adjacent sediments.

In figure 4, a more detailed picture of the vertical distribution of fluid saturations is given for boreholes 978 and 981. Porosity and median particle-size profiles are also plotted in figure 4. These cores, which are at the flanks of the lens, show that oil saturations are highest in the capillary fringe above the water table. At borehole 981 there are also fingers of high oil saturation below the water table which may be related to oil entrapment during water-table fluctuations. The observed annual amplitude of water-table fluctuations is 0.15 to 0.25 m, and, in October 1989, water levels were below the annual mean. The zones of high oil saturation below the water table might also result from lateral migration of oil fingers from upgradient high oil saturation zones related to heterogeneity.

Numerical Simulations

This detailed data set provides an excellent test case for numerical models of multiphase flow. Simulation of multiphase flow requires knowledge of the characteristic functions relating pressures, saturations, and relative permeabilities. Two-and three-phase retention curves for air, oil, and water systems have been determined experimentally (Lenhard and Parker, 1988, Ferrand and others, 1990). Less is known regarding relative permeability functions, especially for three-phase systems. The saturation data obtained in this study allow models of three-phase systems to be tested.

A vertical two-dimensional, numerical model that simulates the flow of oil and water was developed. A mass-balance equation is solved for each fluid phase (Aziz and Settari, 1979):

$$\frac{\partial(\phi\rho_\alpha S_\alpha)}{\partial t} = \nabla\cdot\frac{[k\rho_\alpha k_{r\alpha}}{\mu_\alpha}(\nabla p_\alpha + \rho_\alpha g\nabla z)] + q_\alpha, \quad (1)$$

where α indicates the oil or water phase;

ϕ	is the porosity;
ρ_α	is the density of the a phase (M/L^3);
S_α	is the volumetric saturation of the α-phase;
t	is time (T);
k	is the intrinsic permeability (L^2);
$k_{r\alpha}$	is the relative permeability of the α-phase;
μ_α	is the dynamic viscosity of the α-phase (M/LT);

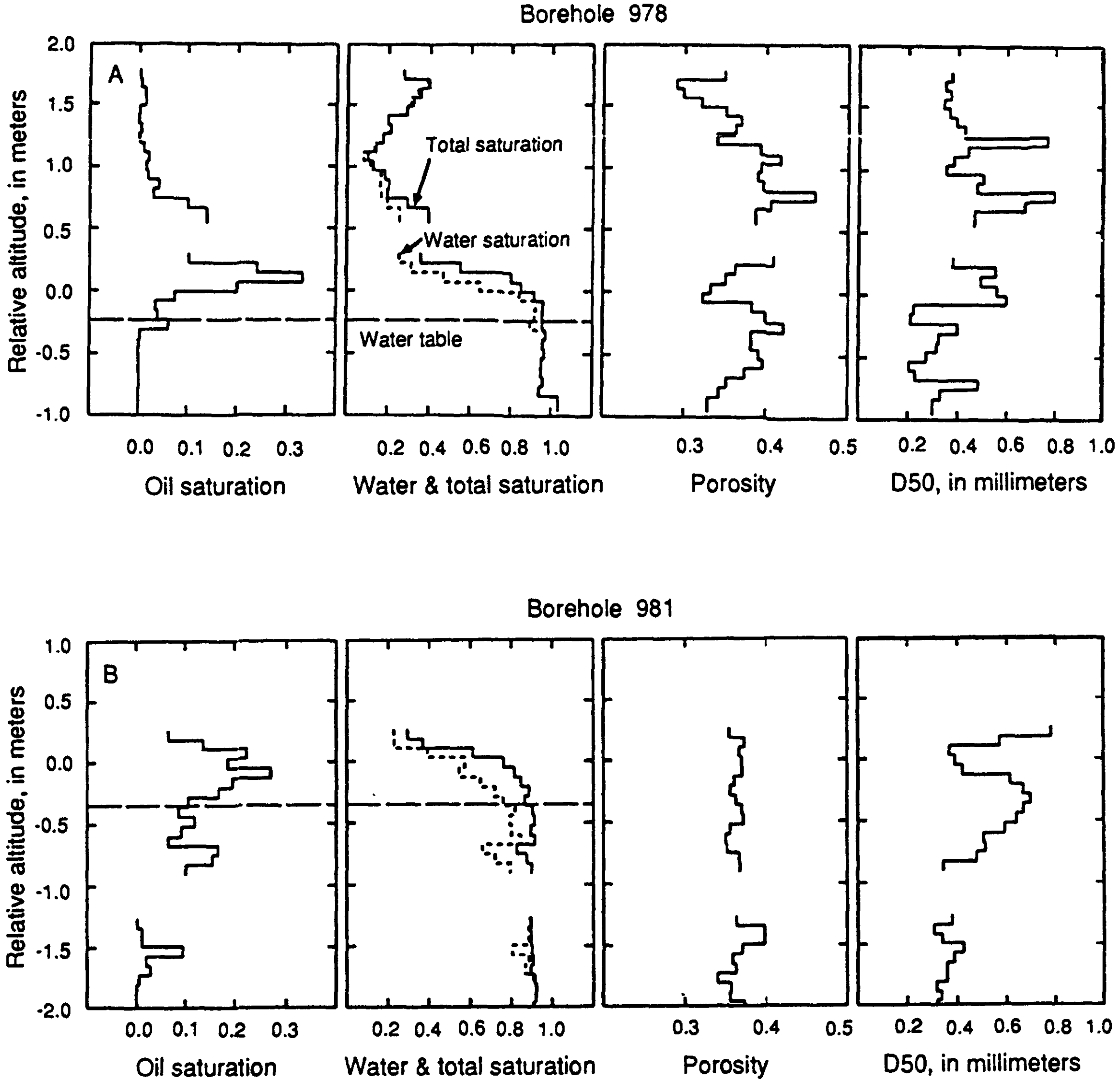


Figure 4. Plots of oil, water and total (oil plus water) saturations, porosity, and median grain size (D50); A. borehole 978, B. borehole 981.

p_α is the fluid pressure of the α-phase (M/LT^2);
g is gravitational acceleration (L/T^2);
z is elevation (L); and,
q_α is a fluid source/sink term (M/L^3T).

Air in the pore space was assumed to be at atmospheric pressure. To solve these equations, the relations between capillary pressure (nonwetting-phase pressure minus wetting-phase pressure) and saturation, and between relative permeability and saturation, must be known. To simplify the calculations, the following hypotheses of Leverett (1941) were adopted. Water saturation was assumed to be only a function of the oil-water capillary pressure, and air saturation was assumed to be only a function of the air-oil capillary pressure. Relative permeability to water was assumed to depend only on water saturation, but oil relative permeability was assumed to be a function of both water and air saturations. Van Genuchten functions were used for the retention and relative-permeability curves (Van Genuchten and Nielsen, 1985), and oil-water and air-oil retention curves were scaled from the air-water curve using measured surface tensions (Lenhard and Parker, 1988). Air-water curves were estimated from particle-size distributions by the method of Arya and Paris (1981). The model of Land (1968) was used to estimate oil entrapment during water imbibition. The objective of the numerical simulation was to determine whether the use of these approximations and estimates (given their uncertainties) could generate a simulated oil lens with the features of the observed lens.

The numerical model was used to simulate 10 years of oil movement along the southern pool transect following the 1979 crude-oil spill. The initial condition for the simulation was a hydrostatic water-pressure distribution corresponding to the measured water-table elevation. The boundary conditions used in the model are illustrated in figure 5A. The lateral and bottom boundaries were set at a constant water pressure. Oil infiltration was distributed across the top of the cross section (as shown in fig. 5A) and held constant for 7 days. It was then discontinued, allowing redistribution of the introduced oil. The actual oil-infiltration conditions following the spill are not well known; however, this representation of the oil spill introduces the estimated volume of oil observed along the transect and reproduces its approximate distribution in the subsurface. The extent of the oil after 7 days of infiltration is shown in figure 5A.

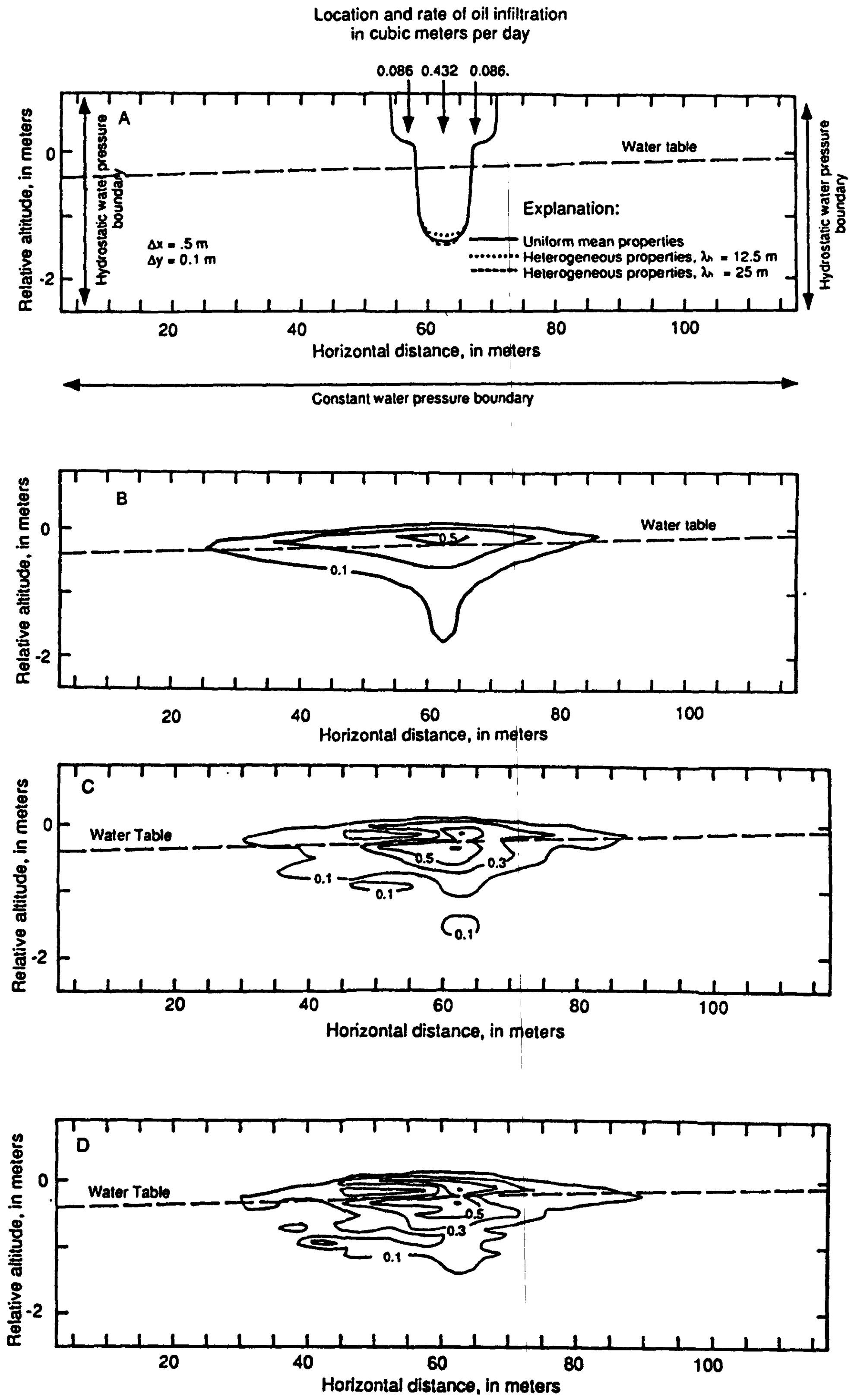


Figure 5. Plots of simulated oil saturations after 10 years of oil movement (contour interval = 0.2). A. Boundary conditions and the 0.1 oil saturation contour after 7 days of infiltration, B. Uniform mean properties; C. Heterogeneous properties, λ_h = 25 m, λ_v = 0.5 m, D. Heterogeneous properties, λ_h = 12.5 m, λ_v = 0.25 m.

As a first approximation, a uniform mean retention curve was used in the model. A uniform permeability of $5 \times 10^{-12} m^2$ (meter squared) was used in this simulation. This value is lower than the mean estimated from particle-size distributions ($2 \times 10^{-11} m^2$) using the relation by Krumbein and Monk (1942); however, higher values led to movement of the oil as far as borehole 982, where no oil was detected during coring. The simulated lens obtained using uniform mean properties is shown in figure 5B. The model predicts that there is a deep finger of oil below the center of the lens. This oil entered the saturated zone during the initial infiltration event and was entrapped during oil redistribution. Unfortunately, no field core penetrates this part of the lens to test this hypothesis. In contrast to the field data, the simulated lens has a smooth distribution of oil with no lateral fingering.

The lack of agreement between this simple model and the observed oil-lens data could have resulted from the use of uniform mean properties of the sediment. To obtain a more realistic representation of the system, a method for incorporating some spatial dependence of the model parameters was developed. Sample permeabilities were estimated from particle-size data (Krumbein and Monk, 1942), and variograms were constructed (Journel and Huijbregts, 1978). Assuming that the permeability (k) is log-normally distributed, the variance of ln(k) at the site is 0.4 and the vertical correlation length is 0.25 to 0.5 m. Estimates of the horizontal correlation length could not be obtained from the horizontal variogram, implying that the horizontal correlation length may be smaller than the average distance between the cores or that not enough data have been collected to sufficiently define the horizontal variogram. To examine the effect of heterogeneity on the oil lens, two simulations with heterogeneous permeability distributions conditioned to the field values were carried out. The Van Genuchten retention-curve parameters were correlated to the ratio $\ln(k)/\ln(\bar{k})$, where $\bar{k}$ is the mean permeability. In the first simulation, the vertical (λ_v) and horizontal (λ_h) correlation lengths were 0.5 and 25 m., respectively (fig. 5C). In the second simulation, both correlation lengths were halved (fig. 5D). The results of simulations indicate that oil movement is quite sensitive to the heterogeneity in sediment structure. Comparison of the simulated and observed oil lenses suggests that further data are needed to characterize the true correlation structure of the sediment properties.

Table 1 lists the first and second spatial moments of the observed and simulated oil lenses. For all simulations, the simulated location of the center of mass is close to that of the observed lens because it depends mainly on the location of oil infiltration and the water-table position. The second moments, σ_{xx} and σ_{yy}, represent the degree of spreading in the horizontal and vertical dimensions, respectively. The simulations obtained using mean properties and hetereogeneous properties underestimate the lateral spreading of the lens (σ_{xx}). This may indicate that the mean permeability used in these simulations is lower than the actual aquifer mean permeability. Lateral spreading of the lens decreases with increasing heterogeneity due to the decreasing continuity in the horizontal dimension. All three simulations underestimate the vertical spreading of the lens (σ_{yy}), probably because water-table fluctuations are not accounted for in the simulations. The simulated vertical finger of entrapped oil beneath the oil lens contains a small mass of oil relative to the total mass in the lens and, therefore, has a small effect on the value of σ_{yy}. None of the simulated lenses successfully reproduce the spreading of oil within the capillary fringe, suggesting that the representation of the three-phase characteristic functions and relative permeabilities may not be adequate.

Table 1. *First and second moments of the observed and simulated oil lenses*

	Center of mass		Second moments	
	x (m)	y (m)	σ_{xx}	σ_{yy}
Observed lens	59.0	-0.36	266	0.209
Uniform mean properties	58.1	-.31	153	.147
Heterogeneous $\lambda h = 25$ m	58.5	-.33	125	.140
Heterogeneous $\lambda h = 12.5$ m	59.4	-.33	118	.154

SUMMARY

A methodology for determining oil, water, and air saturations was developed and applied at a crude-oil spill site near Bemidji, Minn. Cores collected from seven locations along a 120-m longitudinal transect show that a clearly defined oil lens floats on the water table. The zone of high oil saturations is very localized and has depressed the water table. The flanks of the lens are migrating within the capillary fringe. A numerical multiphase flow model was used to simulate the fluid distributions observed along the transect; the model incorporated uniform mean properties and observed heterogeneity. The simulated oil lenses reproduce the general features of the observed oil lens; however, the model is not able to reproduce the details of the subsurface oil distribution.

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FIELD VALIDATION OF CONCEPTUAL MODELS OF MOBILIZATION AND TRANSPORT OF VOLATILE PETROLEUM DERIVATIVES IN THE UNSATURATED ZONE NEAR BEMIDJI, MINNESOTA

By Marc F. Hult[1], Matthew K. Landon[1], *and* Hans-Olaf Pfannkuch[2]

ABSTRACT

A conceptual model of the mobilization, transport, and fate of volatile petroleum hydrocarbons in the unsaturated zone at the site of a crude-oil spill near Bemidji, Minnesota, is presented. The model is based on field data from long-term, interdisciplinary research that began at the site in 1983. The major features of the contaminant plume in the unsaturated zone can be explained by assigning each major chemical constituent to one of three groups based on their sources, transport paths, and fate: (1) C3-C8 alkanes, (2) benzene and alkybenzenes, and (3) methane. C3-C8 alkanes are the least complex group. They comprise about 85 percent of the contaminant mass; their source can be characterized by a single partitioning term, and their movement is not strongly coupled with ground-water flow because water/soil-gas interchange is not a major process. Benzene and alkybenzenes are of intermediate complexity. Their high aqueous solubility causes them to partition to and be transported with ground water. Consequently, oil/gas, oil/water and gas/water partitioning and concentrations in ground-water must be known. The most complex group consists in methane, which is produced in the unsaturated and saturated zones under anaerobic conditions. Therefore, two biologic rates need to be specified, which, in turn, depend on substrate concentrations controlled by saturated- and unsaturated-zone processes.

INTRODUCTION

Modeling the mobilization, transport, and fate of volatile hydrocarbons in the unsaturated zone requires an understanding of the interactions among water, oil, soil gas, and sediment. A conceptual model of the mobilization, transport, and fate of volatile petroleum hydrocarbons in the unsaturated zone is presented on the basis of field data collected during long-term, interdisciplinary research begun in 1983 at a site near Bemidji, Minn. (fig. 1). Crude oil spilled in 1979 is floating on the water table about 8 m (meters) below land surface in a glacial outwash aquifer (Hult, 1984). The oil is dissolving in ground water and vaporizing in the unsaturated zone.

Hult and Grabbe (1986) measured the distribution of individual organic compounds in soil-gas samples using gas chromatography with flame-ionization and photo-ionization detectors. Total volatile hydrocarbon (TVH) concentrations also were determined. TVH is a lumped-parameter measurement that can be used to determine the distribution of organic carbon in the unsaturated zone. It is analogous to the measurement of dissolved organic carbon in the saturated zone.

The distribution of TVH in the unsaturated zone along a section that crosses an oil body and is aligned parallel to the direction of ground-water flow is shown in figure 2A. Concentrations of TVH measured directly above the oil were comparable to those measured in the headspace in a tightly sealed bottle of oil, indicating that the oil/soil gas contact was in equilibrium. The concentrations decreased by about five orders of magnitude in a vertical distance of 8 m. The distribution of the partial pressure of carbon dioxide parallels that of TVH. The distribution of oxygen (fig. 2B) decreases monotonically from away from the zone of high concentrations of carbon dioxide.

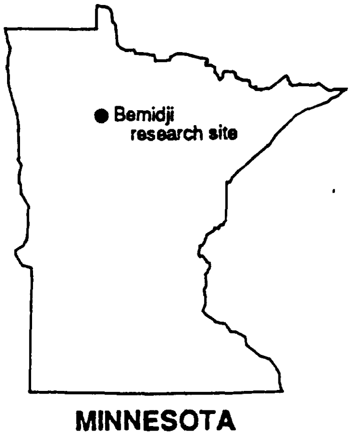

Figure 1. Location of Bemidji research site, Minnesota.

The consistent relation between TVH concentrations and the partial pressures of oxygen and carbon dioxide is presumed to be caused by biologically mediated oxidation. Removal of hydrocarbons appears to be virtually complete as shown by the chromatograms in figure 3. If all of the TVH had been derived from the spill of a single, sparingly soluble compound, these data would suffice for calibration of a transport model incorporating a liquid/gas partition coefficient for the source term. This shows the usefulness of a noncompositional approach. However, a noncompositional model has serious limitations. For example, methane (fig. 2C) is not a significant component of the source oil, as shown by the chromatograms of the headspace of two samples of oil (fig. 3) and, therefore, cannnot be specified as a source term by using oil/gas partition coefficients. It is a degradation product of the oil produced under anaerobic conditions in both the unsaturated and saturated zone and is itself subject to oxidation.

MOBILIZATION OF HYDROCARBONS

The source oil is a complex mixture containing compounds with widely differing properties. Landon and Hult (this Proceedings) demonstrate that the oil was originally of virtually uniform composition and that differences in

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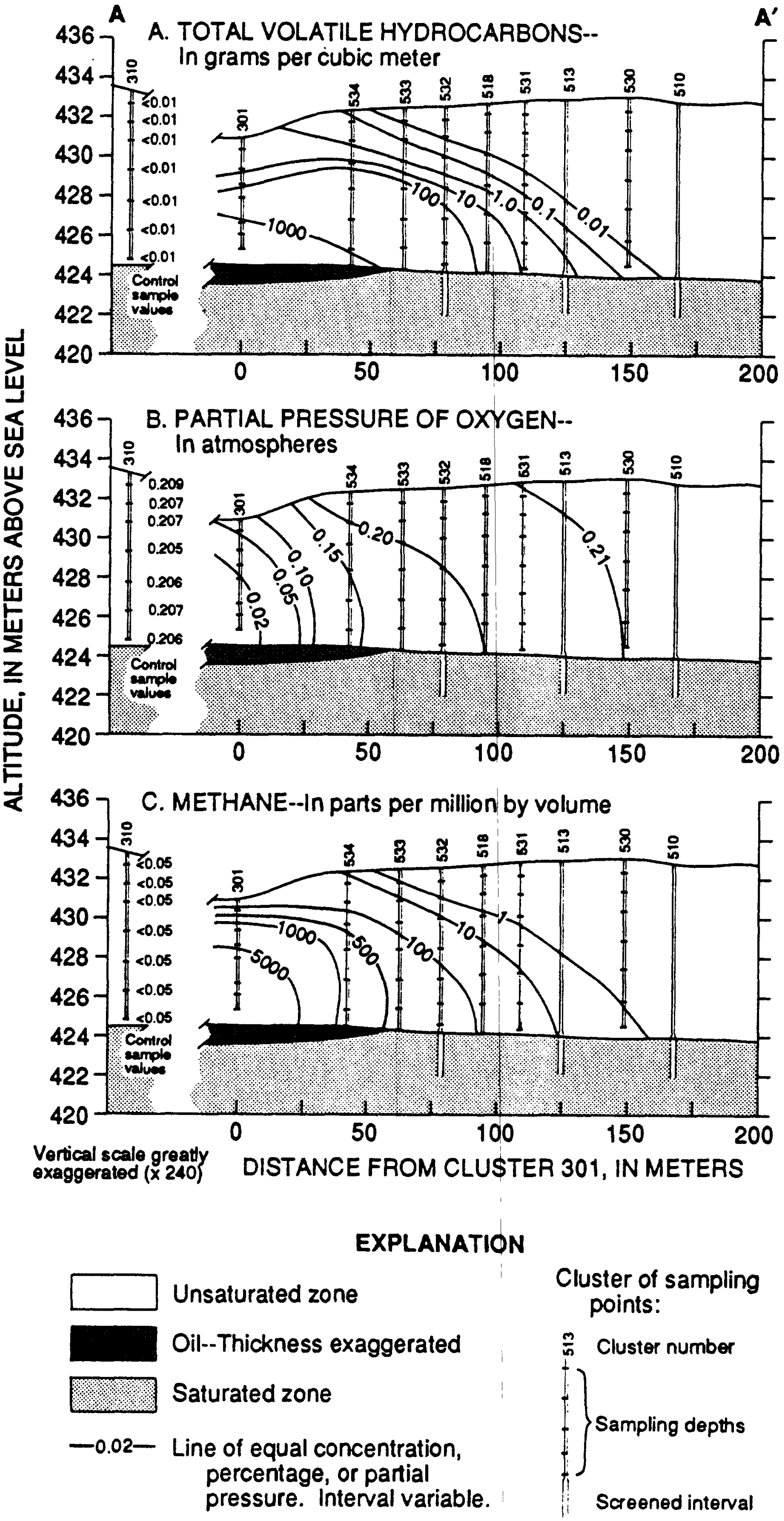

Figure 2. Sections showing distribution of total volatile hydrocarbons, oxygen, and methane in vapor in the unsaturated zone.

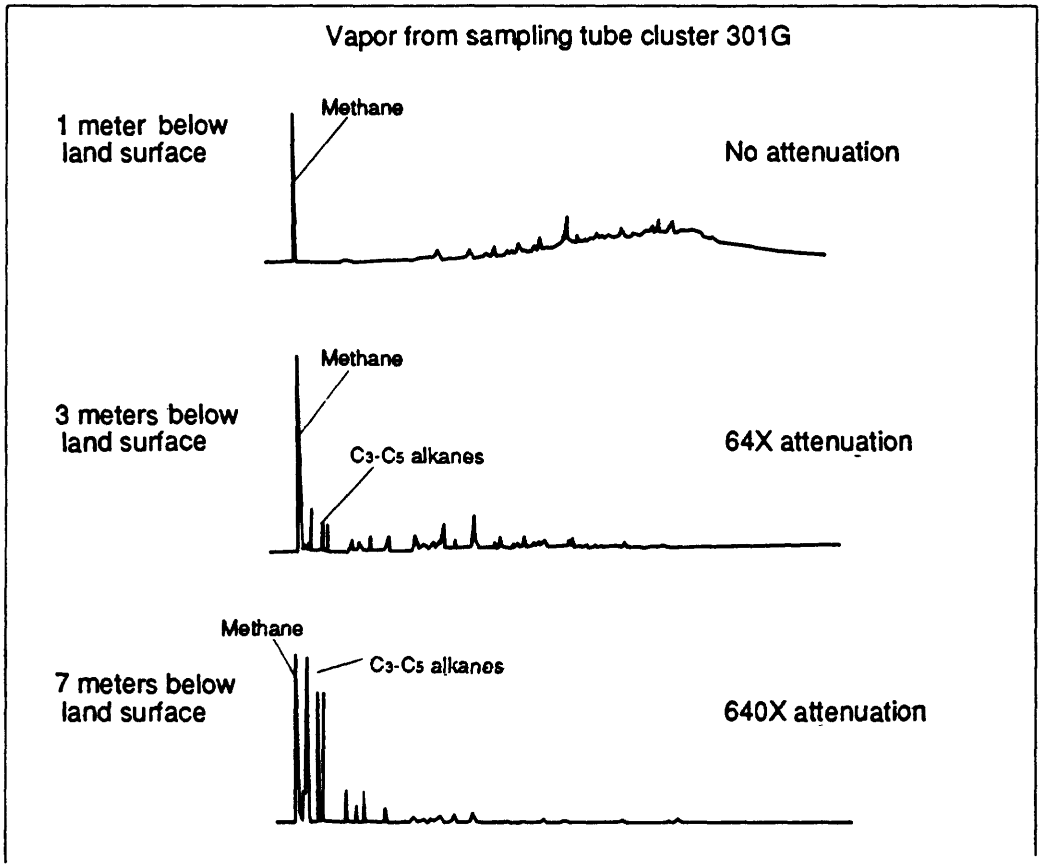

Figure 3. Chromatograms showing change in composition and concentration with depth of hydrocarbon vapors in the unsaturated zone.

composition are mirrored by differences in physical properties that can be used to estimate the percentage lost from a given sample. The chromatograms (fig. 4) show that the oil samples have differentially lost volatile constitutents. The oil samples from wells 316 and 309 are representative of the least and most altered oils, respectively. The percentages of C3-C5 normal and branched alkanes differ widely in oil samples from each well, but the percentages of C6 and higher compounds are very similar in oil samples from each well.

The physical characteristics of a homologous series of compounds and, therefore, its transport and fate, which depends on those characteristics, differ systematically. The relation among the molecular weight of normal alkanes and selected aromatic compounds and Henry's Law constants is shown in figure 5. Vapor pressure controls oil/gas partitioning. Aqueous solubility controls dissolution and therefore oil/water partitioning. The Henry's Law constant is the ratio of vapor pressure to solubility and, therefore, controls whether a given compound preferentially partitions from the oil to ground water or to soil gas. The alkanes strongly partition to soil gas and aromatic compounds strongly partition to water.

Crude-oil vapors are simple compared to those of light petroleum distillates, such as gasoline, because compounds created by refining are not present. Nearly all of the organic substances measured in soil gases at Bemidji can be accounted for by three groups on the basis of their origin and physicochemical properties: (1) C3-C8 normal, branched, and methylalkanes; (2) benzene and alkylbenzenes; and (3) methane (and biogenic ethylene and ethane, if present). Each homologous series of alkanes behaves similarly to those shown. The major alkylbenzenes fall very near the line between benzene and naphthalene. Not accounted for are cycloalkanes, which are intermediate in properties to the alkanes and aromatic compounds, and low-molecular-weight organic acids, which typically have low response factors on a flame-ionization detector.

On the basis of the Henry's Law coefficients, the alkanes should preferentially vaporize to the soil gas and move away in all directions through the unsaturated zone by diffusion. Aromatic compounds should preferentially dissolve and move with ground water. Methane is created by anaerobic degradation in both the saturated zone and the unsaturated zone and so will be present in both locations. Because of its hydrophobicity, it will tend to repartition from water to soil gas at the water table. Figure 6 shows representative chromatograms of samples that illustrate this point. The upper chromatogram shows the composition of soil gas above the water table at well cluster 518 (fig. 2A). The lower chromatogram shows the composition of water from water-table well 518. The soil gas is primarily composed of alkanes, including methane. The water composition is dominated by methane and aromatic compounds. Compared to soil gas near the oil, this sample contains a greater proportion of benzene, presumably owing to transfer of benzene from the water to the soil gas.

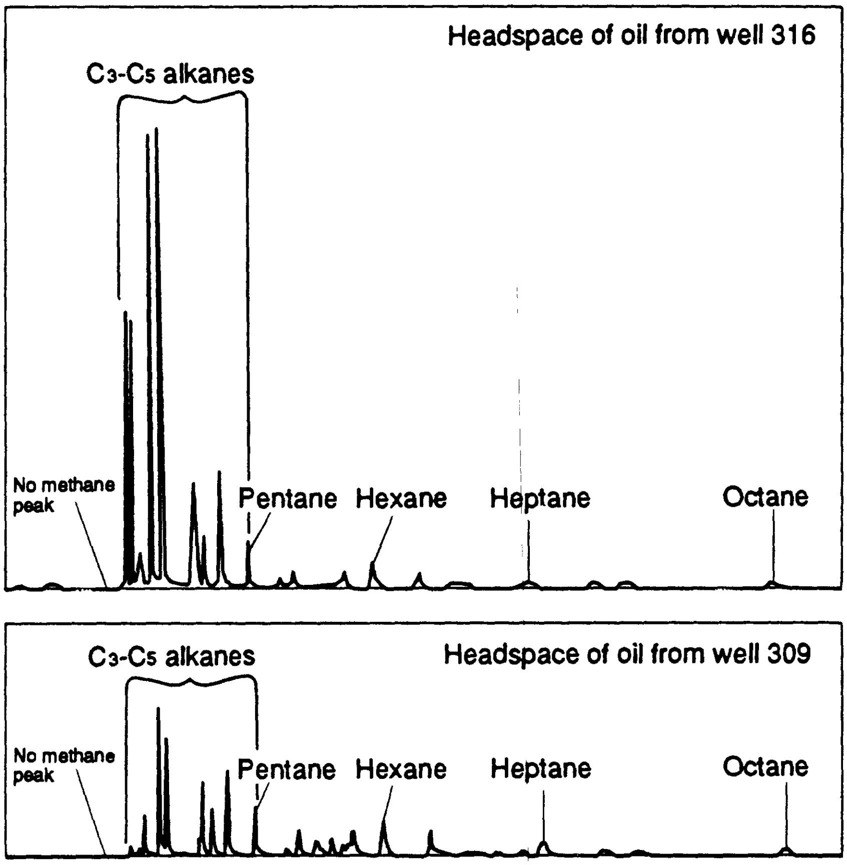

Figure 4. Chromatograms of the headspace of two representative oil samples showing differential loss of alkanes.

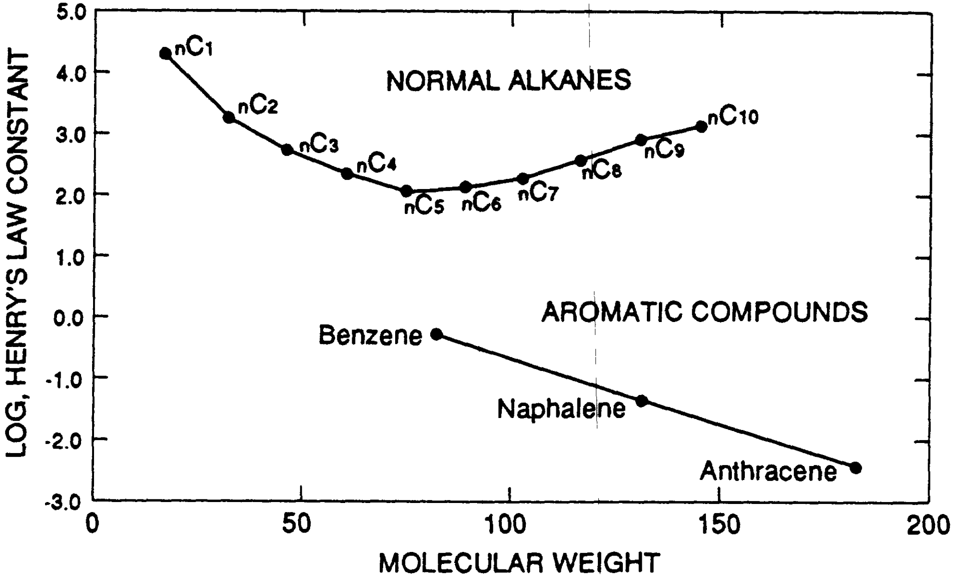

Figure 5. Graph showing Henry's Law constants for normal alkanes and selected aromatic compounds.

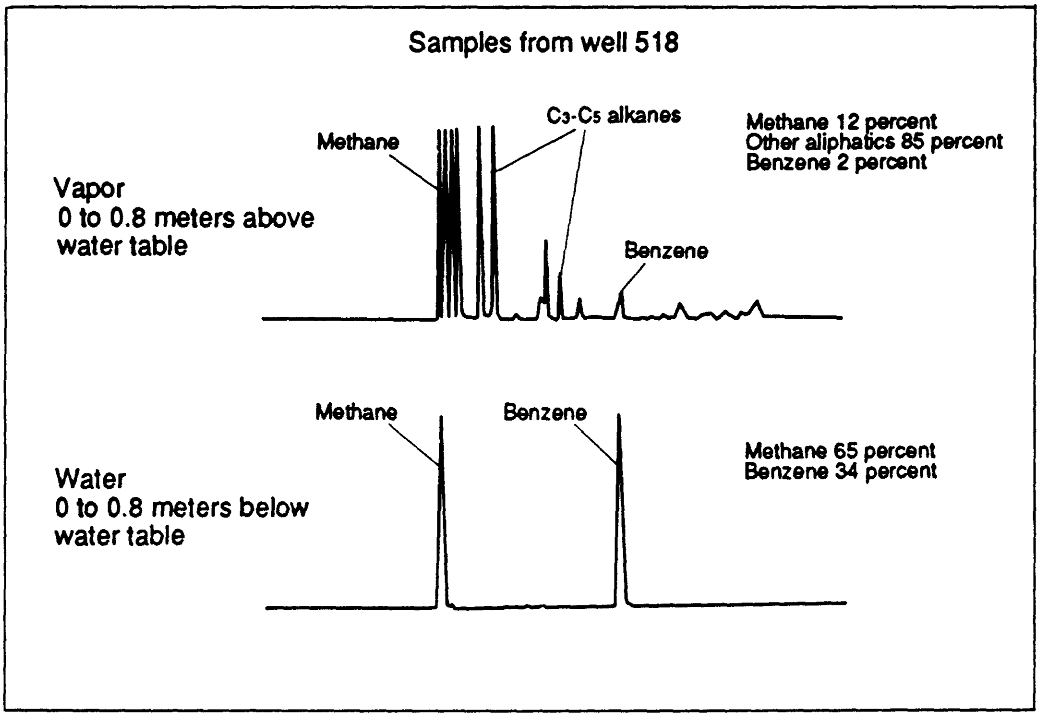

Figure 6. Chromatograms showing difference in hydrocarbon composition bewteen water and soil vapor samples taken near the water table.

CONCEPTUAL MODELS

The major features of the contaminant plume in the unsaturated zone can be explained by assigning each major chemical constituent to one of three groups: (1) C3-C8 alkanes, (2) benzene and alkybenzenes, and (3) methane. The regularity and predictability of the transport and fate behavior of a homologous series of compounds makes this conceptual model useful for comparing relative transport of individual hydrocarbons. Although all partitioning and transport processes can occur at diminishingly small rates, and, therefore, errors are introduced if these processes are neglected, this approach can provide an acceptable level of simplification needed for developing the conceptual models on which to base numerical models.

The C3-C8 alkanes have the least complex behavior and are, therefore, easiest to simulate. They typically comprise about 85 percent of the contaminant mass, the source can be characterized by a single oil/water partitioning term, and their movement is not strongly coupled with ground-water flow because water/soil gas interchange is not a major factor. Oxidation is virtually complete in the unsaturated zone so losses to the atmosphere are negligible. Consequently they can be realistically modeled as a closed system with vapors moving by diffusion and advection from a single stationary source.

The behavior of benzene and alkybenzenes is of intermediate complexity. Their high aqueous solubility causes them to partition to, and be transported with, ground water. Consequently oil/gas, oil/water, and gas/water partitioning and their spatial distribution in ground water need to be specified. The distribution in the unsaturated zone may be modified by percolating recharge. This may require coupled ground-water/unsaturated zone transport modeling. Like the alkanes, oxidation is virtually complete in the unsaturated zone. However, the compounds are of regulatory and environmental concern at much lower concentrations than the alkanes.

The behavior of methane is the most complex. It is produced both in the unsaturated and saturated zone under anaerobic conditions. Therefore, two biologic rates need to be specified, which, in turn, depend on substrate concentrations controlled by saturated- and unsaturated-zone processes rather than by simple partitioning. The distribution is coupled with ground-water flow. It appears (fig. 3) that significant amounts of methane escape to the atmosphere so the system is not closed with respect to methane, which complicates specification of the upper boundary condition.

SUMMARY

Field data on (1) the distribution of total volatile hydrocarbons, oxygen, and carbon dioxide in soil gas; (2) the composition of hydrocarbon vapors partitioning from oil and water; and (3) the relative distribution between ground water and soil gas of individual organic compounds were used to construct conceptual models of three major groups of hydrocarbons moving through the unsaturated zone at a research site near Bemidji, Minn.

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GEOCHEMICAL MODELING OF ORGANIC DEGRADATION REACTIONS IN AN AQUIFER CONTAMINATED WITH CRUDE OIL

By Mary Jo Baedecker[1] *and* Isabelle M. Cozzarelli[1]

ABSTRACT

Crude oil from a pipeline break accumulated as an oil body at the water table in an aquifer near Bemidji, Minnesota. Hydrocarbons from crude oil were transported downgradient and a contaminant plume formed. The chemical composition of the ground water in the contaminant plume was significantly changed by the aerobic and anaerobic degradation of hydrocarbons and dissolution and precipitation of minerals. The mass transfer for chemical reactions that occurs at a point beneath the oil body to 40 meters downgradient from the oil body is calculated. The results of the mass-transfer calculations indicate that the major processes are the degradation of hydrocarbons; loss of carbon dioxide and methane to the unsaturated zone and into the atmosphere; dissolution of calcite and iron and manganese oxides; and precipitation of silica and an iron-rich carbonate.

INTRODUCTION

Crude oil from a pipeline break accumulated as an oil body at the water table in a glacial-outwash aquifer near Bemidji, Minnesota (fig. 1). Several processes affect the distribution and fate of the organic compounds that are components of the crude oil. These processes include the movement of ground water, and the dispersion, volatilization, sorption, and biodegradation of the organic compounds. Many investigations have reported processes of alteration of crude oil in surface waters and in petroleum reservoirs. Few investigations have been undertaken to determine the fate of crude oil and the geochemical effects of its degradation in an aquifer. Other geochemical investigations have reported that concentrations of aqueous species change significantly in plumes that develop from the transport and degradation of organic compounds (Baedecker and Back, 1979; Nicholson and others, 1983; Barker and others, 1986; and Lesage and others, 1990).

Geochemical modeling describes the interaction of water with the solid media along an evolutionary reaction path (Plummer, 1984). In contaminated aquifers the degradation of organic compounds results in large changes in the distribution of aqueous species over short distances vertically and horizontally. Quantitative information for the amount of mass transfer along a flow path will improve predictive tools for the management of toxic-waste sites.

The purpose of this paper is to describe the dominant geochemical processes along a flow path from beneath the crude oil to 40 m (meters) downgradient from the oil body. Considering the geochemistry of the crude oil, water, and aquifer material, chemical reactions are described quantitatively using a modified version of the model BALANCE (Parkhurst and others, 1982).

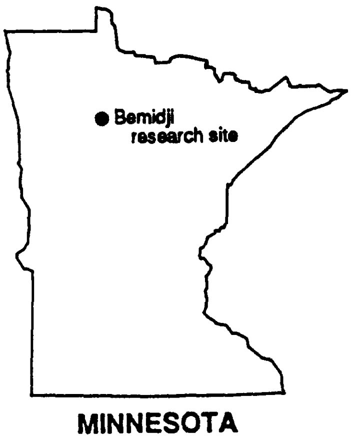

Figure 1. Location of Bemidji research site, Minnesota.

METHODS

The methods used for the determination of chemical constituents that are sensitive to changes in the oxidation state of water are described in Baedecker and Cozzarelli (1991). Water samples collected for analysis of cations and anions were filtered through 0.2 µm (micrometer) filters. The pH, alkalinity, and concentrations of dissolved oxygen were determined in the field. Major cations were analyzed by direct-current plasma emission spectrometry, and anions, other than bicarbonate, were determined by ion chromatography. Dissolved gases were measured by the method described in Pearson and others (1978). For the determination of $\delta^{13}C$ values, the total inorganic carbon was precipitated from ground water samples as strontium carbonate. In the laboratory the precipitate was converted to carbon dioxide (CO_2) and the isotopic composition of carbon in the CO_2 was measured on an isotope-ratio mass spectrometer. Methane was collected for isotopic analysis by removing a sample of the gas phase from the headspace of a mixture of air and water that was allowed to equilibrate. The methane was converted to CO_2 by combustion and its isotopic composition measured. Also, a sample of the crude oil was combusted to CO_2 for isotopic analyses of carbon.

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RESULTS

Site Description

A pipeline that carried crude oil ruptured in 1979 near Bemidji, Minn. Although much of the crude oil was recovered, some of it reached the water table where an oil body formed (Hult, 1984). The aquifer, in glacial outwash, is a well-sorted, medium quartz sand containing about 6 percent carbonate minerals, 30 percent feldspars, less than 5 percent clay minerals, and less than 0.2 percent organic carbon. The water table is 5 to 7 m below land surface.

The boundaries of the plume, illustrated for the distribution of total dissolved organic carbon (TDOC) in figure 2, show that the plume is narrow and that the contaminants were transported about 180 m downgradient from the middle of the oil body. Organic compounds in concentrations of less than 0.2 microgram per liter may extend beyond 180 m. The TDOC data include volatile and nonvolatile organic carbon from water that was filtered through a 0.2 µm filter. A section through the plume (fig. 3) shows the depth and location of the anoxic zone that has high concentrations of organic and inorganic constituents (Baedecker and others, 1989).

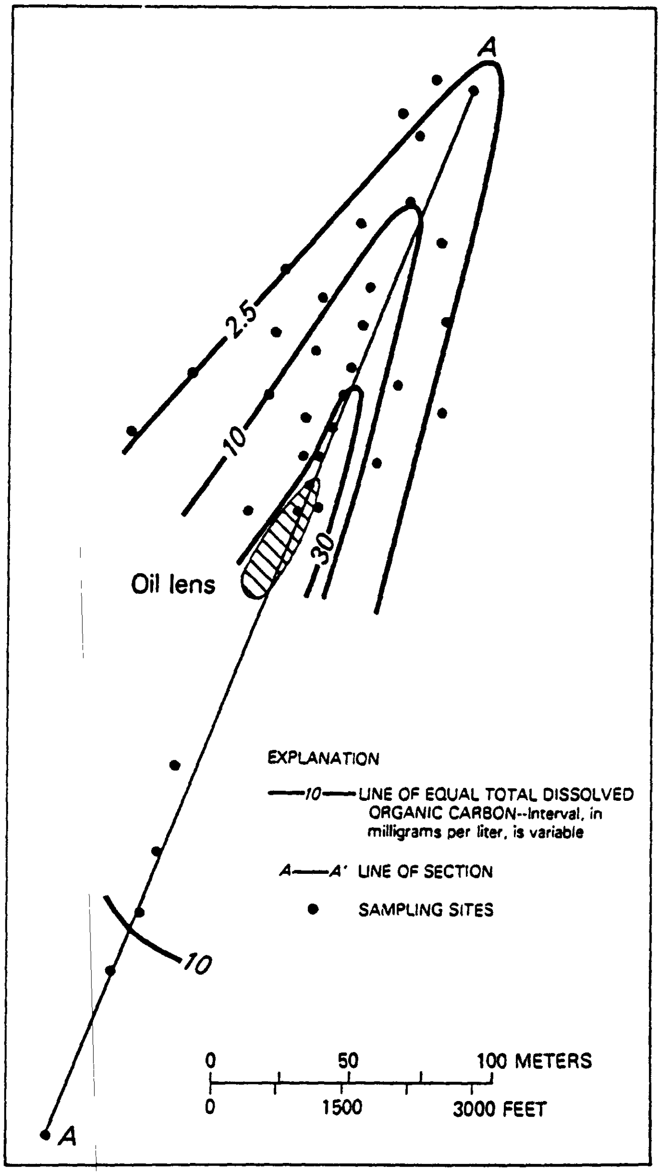
A
2.5
10
30
Oil lens
10
A
EXPLANATION
—10— LINE OF EQUAL TOTAL DISSOLVED ORGANIC CARBON--Interval, in milligrams per liter, is variable
A——A' LINE OF SECTION
● SAMPLING SITES
0
50
100 METERS
0
1500
3000 FEET

Figure 2. Contaminant plume using the concentrations of total dissolved organic carbon (TDOC), in milligrams per liter. Direction of ground water flow is to the northeast. A localized area of high TDOC values upgradient from the oil body is the result of overland spray of the crude oil.

Geochemistry of the Oil, Water, and Sediment

The crude oil at the water table is a paraffinic oil composed primarily of hydrocarbons in the C_1 to C_{35} range (n in C_n refers to the number of carbon atoms in a compound). The aromatic hydrocarbons, benzene and the alkylbenzenes (C_6 to C_{10}), are soluble in water and were present in ground water 200 m downgradient of the oil body. The aromatic hydrocarbons are degraded in ground water by microbial processes (Eganhouse and others, 1987; Cozzarelli and others, 1990; Baedecker and Eganhouse, 1991). Along a 20-m-long flow path downgradient from the oil, the concentrations of hydrocarbons (aromatic and aliphatic) decreased by 40 to 99 percent.

Data for the distribution of aromatic hydrocarbons indicate that some of the compounds are degraded in an anoxic zone that extends 75 m downgradient of the oil body (fig. 3). In the middle of the anoxic zone beneath the oil body, calculated Eh (redox) measurements from the sulfate/sulfide (SO_4^{2-}/S^{2-}) and bicarbonate/methane (HCO_3^- /CH_4) couples were -0.165 and -0.221 volts, respectively. High concentrations of reduced aqueous species were found in ground water at this location. Concentrations of ferrous iron (Fe^{2+}) and CH_4 were 1.05 and 1.36 mmol/L (millimoles per liter), respectively. The concentrations of SO_4^{2-} were low and, thus, only small amounts of hydrogen sulfide (H_2S) were found. H_2S that formed would precipitate from solution as iron sulfides because the concentrations of Fe^{2+} are high. Additional evidence for the degradation of aromatic hydrocarbons was the identification of organic acids in anoxic ground water that were structurally related to the hydrocarbons and are probably intermediates in the degradative processes (Cozzarelli and others, 1990). These acids were found only in the anoxic water zone. Laboratory microcosm experiments, conducted using sediment and water from the site, verified that benzene and some of the alkylbenzenes are degraded under anoxic conditions. Also, toluene was degraded by an iron- reducing bacterium in the laboratory under anoxic conditions (Lovley and others, 1989).

The degradation of hydrocarbons in the anoxic zone affects the concentrations of organic and inorganic dissolved aqueous species. The pH; concentrations of major cations, anions, and unstable constituents; carbon isotopic data; and saturation indices for selected minerals are presented in table 1 and figure 4 for contaminated ground water at two sites in the anoxic zone. One of the sites is about 2 m below the oil body (A) and the other site is 40 m downgradient from the oil body (B)(fig. 3). The concentrations of the cations decreased from site A to site B, with the exception of Mn^{2+}, which increased (fig 4). The largest decreases in concentrations of aqueous species from site A to site B were for Fe^{2+}, HCO_3^-, TDOC, and CH_4.

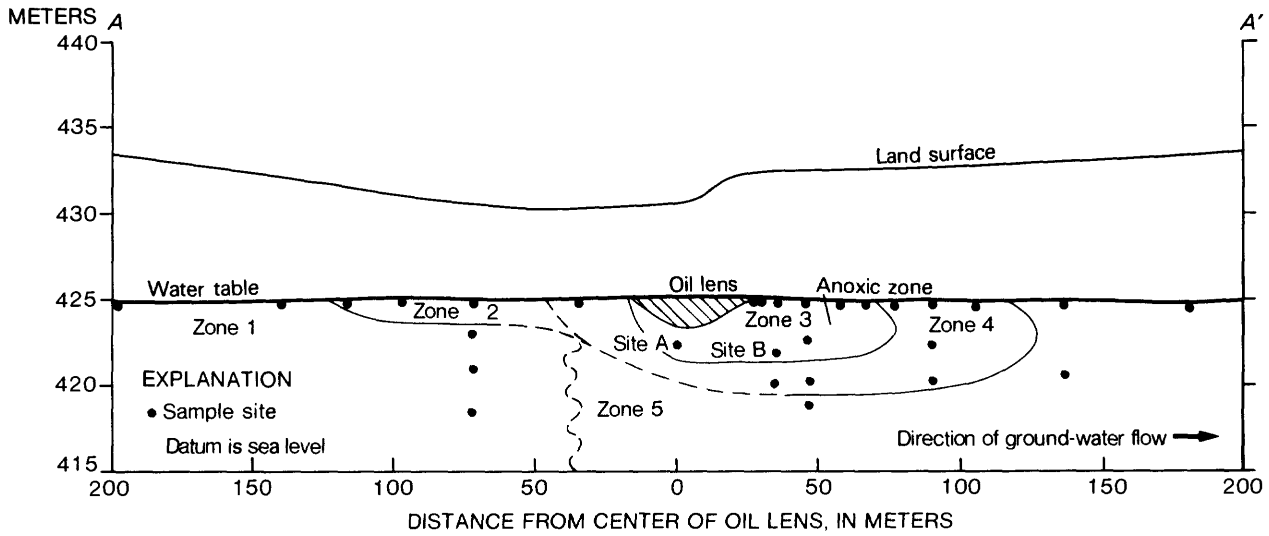

Figure 3. Hydrogeologic section through the contaminant plume (fig. 2) showing the anoxic and low-oxygenated ground water zones of the plume. (Modified from Baedecker and others, 1989.)

Dissolved gases were measured in water from two sites in the anoxic zone (at site A and 2 m vertically upward from site B). The gases identified were nitrogen, oxygen, argon, carbon dioxide, hydrogen, methane, and ethane. The total partial pressures were 1.00 and 0.93 atmospheres at these two sites.

The $\delta^{13}C$ value of the crude oil was -28.40 ‰ (per mil). The $\delta^{13}C$ values for soil gas CO_2 in the uncontaminated aquifer were -21.45 ‰ and above the contaminated water close to the oil body were -24.70 ‰. The $\delta^{13}C$ value of the bulk carbonate from an uncontaminated part of the aquifer was -0.74 ‰ (Philip Bennett, University of Texas at Austin, oral commun., 1991). The $\delta^{13}C$ values for the total dissolved inorganic carbon (TDIC) were -5.80 ‰ at site A and -5.95 ‰ at site B. These values are enriched in ^{13}C as a result of the fractionation of carbon isotopes during methanogenesis, which produced isotopically depleted methane (Baedecker and others, 1989).

Table 1. *Water chemistry[1], isotopic values[2], and mineral saturation indices[3]*

[<, less than; --, no data]

	Site A	Site B
pH	6.78	6.93
O_2	.00	.00
H_2S	<.02	<.02
DOC[4]	33.8	16.2
VOC[5]	16.3	2.0
$\delta^{13}C_{CO_2}$	-5.80	-5.95
$\delta^{13}C_{CH_4}$	-56.1	-53.6
Calcite	-.006	-.040
Dolomite	-.383	-.545
Siderite	1.437	.277
Chalcedony	.712	.422
Quartz	1.256	.971
Kaolinite	6.012	--

[1] In milligrams per liter, except pH. Other data in figure 4.

[2] In parts per thousand relative to PDB standard.

[3] Log (ion activity product/equilibrium constant).

[4] Dissolved organic carbon.

[5] Volatile organic carbon.

Calculations based on thermodynamic principles using the equilibrium speciation model WATEQF (Plummer and others, 1976) indicate that the water at sites A and B is near saturation or undersaturated with respect to calcite and dolomite and supersaturated with respect to siderite, quartz, and kaolinite. In some parts of the plume, quartz dissolution features were observed on quartz grains where ground water was supersaturated with respect to quartz (Bennett and Siegel, 1987). Several sediment samples were analyzed by scanning electron microscopy with energy-dispersive X-ray fluorescence (SEM-EDAX) to examine the carbonates. Calcite, and lesser amounts of dolomite, were found. No siderite was found. However, coatings with more iron than calcium were present on some calcite grains. Thus, Fe^{2+} may be precipitating with Ca^{2+}, and perhaps Mg^{2+}, as a carbonate solid solution.

Geochemical Modeling

The geochemical data and mineralogical information were used to obtain quantitative information for the mass transfer of chemical reactions along a flow path in the anoxic zone. The geochemical model used was a modified version of BALANCE (Parkhurst and others, 1982) that considers the oxidation state and $\delta^{13}C$ values of the organic material in solution and in the aquifer sediment (L.N. Plummer, U.S. Geological Survey, oral commun., 1991). The approach was to use observed data from two points in the aquifer and to specify the major chemical reactions along the flow path between these two points. The two points in the aquifer were a few meters below the oil body (site A) and 40 m downgradient from the oil body (site B). Data for the measured chemical constituents and carbon isotopes in table 1 and figure 4 were used in the model. Concentrations of sodium (Na^+), strontium (Sr^{2+}), aluminum (Al^{3+}), H_2S, chloride (Cl^-), and SO_4^{2-} were low and were not included in the model.

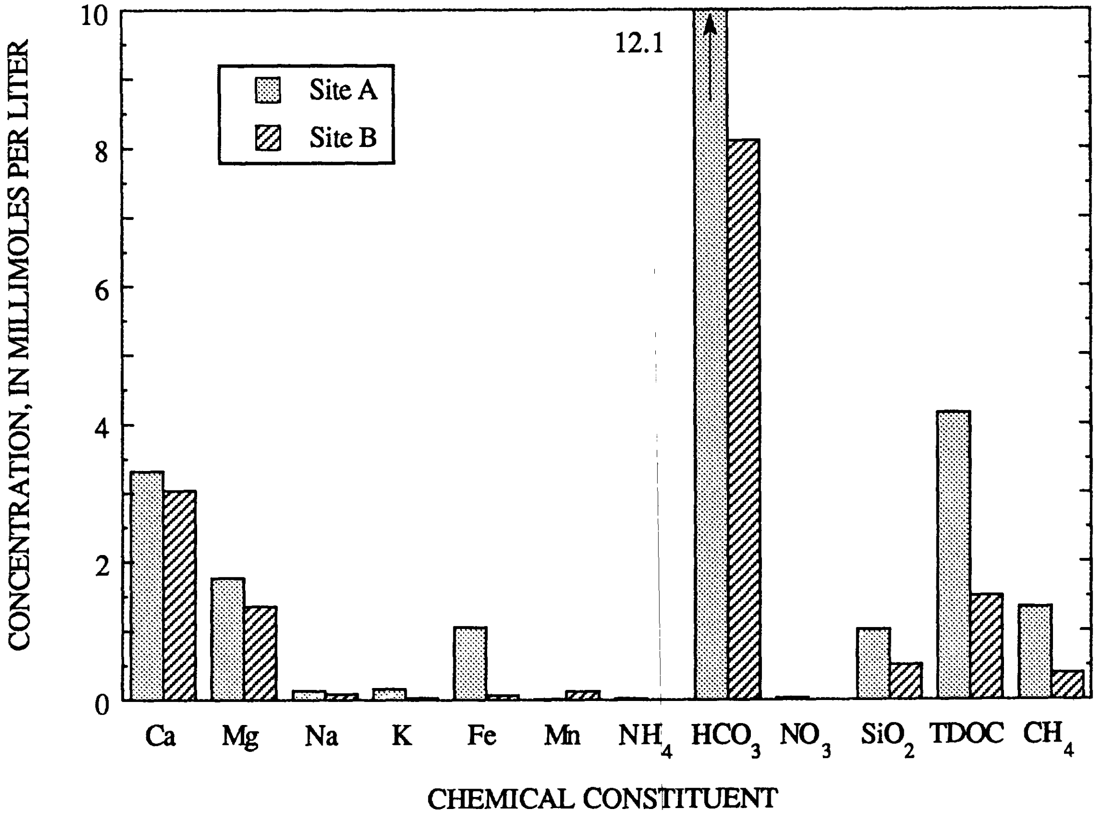

Figure 4. Concentrations of aqueous chemical constituents in ground water from two contaminated sites in the anoxic zone, in 1987. Locations of the sites are shown in figure 3.

Solid phases that were selected to dissolve were Fe and Mn oxides and calcite. Calcite was dissolved to provide calcium (Ca^{2+}) to reprecipitate as a solid solution with Fe^{2+}. A ferroan carbonate of the composition $Fe_{.8}Ca_{.2}CO_3$ was selected to precipitate. Ca may substitute for Fe up to a maximum of about 23 percent (Palache and others, 1951). Silica was precipitated as amorphous silica, however, the mechanism by which silica is removed from solution is unknown. The concentrations of Al^{3+} were low (0.002 mmol/L) which means that to precipitate clay minerals, other clay minerals of a different composition would have to dissolve. The loss in concentration of the cations, NH_4^+, K^+, and Mg^{2+} from water between sites A and B was attributed to ion exchange of NH_4^+ for Ca^{2+} and to sorption of potassium (K^+) and magnesium (Mg^{2+}) on clays.

The most abundant dissolved gases were CO_2 and CH_4. The aquifer was treated as an open system, and the gases could leave the system by outgassing through the unsaturated zone to the atmosphere. The ratio at which these gases leave the system was assigned according to their measured partial pressures in gas in equilibrium with the contaminated ground water (0.131 CO_2 to CH_4).

Values of -25.00 ‰ were assigned for the $\delta^{13}C$ of TDOC, which includes the volatile and nonvolatile organic carbon. The isotopic composition of the volatile organic carbon is probably close to that of the crude oil and possibly even lighter because the light hydrocarbons are generally isotopically depleted compared to the total crude oil (Silverman, 1963), and it is the light hydrocarbons that are soluble in water. The nonvolatile carbon pool may be heavier than the volatile carbon pool because it is the material remaining from degradative processes. The carbon in CO_2 that outgassed was fractionated by about 7 ‰, which was computed in the model from the equilibrium isotopic fractionation factors and the temperature of the water. The CH_4 was outgassed with no fractionation. The Fe-rich carbonate phase was precipitated with a fractionation factor of 1.0 ‰. This factor, calculated by the model, is based on several investigations for the fractionation of carbon in calcite precipitated from a bicarbonate solution (for a review see, Kyser, 1987).

The oxidation state of carbon in TDOC was assigned -1 at site A and 0 at site B. This is because at site A a larger portion of the TDOC is composed of hydrocarbons from crude oil and these compounds are more reduced (oxidation states of -2.3 to -1) than a carbohydrate type organic material, which has an oxidation state of 0.

The results of the model (table 2) show that, quantitatively, in order of the greatest to least amount of mass transfer along a flow path from site A to site B, the primary reactions are the precipitation of an iron and calcium carbonate phase, dissolution of iron oxide, microbial degradation of organic carbon, loss of CO_2 and CH_4, dissolution of calcite, and precipitation or loss of silica. Of lesser importance are the dissolution of Mn oxides, sorption of cations on clays, and ion exchange. The isotopic value computed for the total carbon (organic and inorganic) at site B from the isotopic value at site A and mass transfer reactions

Table 2. *Mass transfer of phases for chemical reactions between Site A and Site B*

[Values in millimoles per liter; $\delta^{13}C$ in parts per thousand, relative to PDB standard; DIC, total dissolved inorganic carbon; TC, total carbon (organic and inorganic)]

Water chemistry at site A		Phases dissolved or exchanged		Phases precipitated or outgassed		Water Chemistry at site B	
Ca^{2+}	3.322					Ca^{2+}	3.046
Mg^{2+}	1.770					Mg^{2+}	1.366
K^+	.169					K^+	.036
Fe^{2+}	1.055	1.58	Calcite	0.298	CO_2	Fe^{2+}	.079
Mn^{2+}	.016	.112	MnO_2	1.98	CH_4	Mn^{2+}	.127
NH_4^+	.028	.013	$Ca^{2+}$for NH_4^+	9.35	$Fe_{.8}Ca_{.2}CO_3$	NH_4^+	.0054
SiO_2	1.018	6.50	$Fe(OH)_3$	.510	Si_{amp}	SiO_2	.508
HCO_3^-	12.058			.133	K sorbed	HCO_3^-	8.118
TDIC	17.004			.404	Mg sorbed	TDIC	10.576
NO_3^-	.036					NO_3^-	.000
TDOC	4.170					TDOC	1.516
CH_4	1.356					CH_4	.388
TC	22.53					TC	12.48
$\delta^{13}C_{TC}$	-12.38					$\delta^{13}C_{TC}$	-9.74
$\delta^{13}C_{TDIC}$	-5.80					$\delta^{13}C_{TDIC}$	-5.95

$\delta^{13}C_{TC}$ calculated at Site B (Site A + change from reactions) = -9.85
$\delta^{13}C_{TDIC}$ calculated at Site B (Site A + change from reactions) = -6.09

is -9.85 ‰. The observed value at site B is -9.74 ‰. Likewise, the isotopic value computed for the total inorganic carbon at site B is -6.09 ‰, whereas the observed value is -5.95 ‰.

The results of the model are significant to understanding the geochemical processes at Bemidji. The cycling of large amounts of Fe- containing minerals, the dissolution of Fe oxides and precipitation of Fe in carbonates result in long-term changes in the mineralogy of the aquifer. The dissolution of Fe oxides is coupled with the degradation of organic compounds, and this is a major process by which organic compounds are attenuated in contaminated aquifers. Another major process is methanogenesis as shown by the high concentrations of CH_4 and the large enrichment of $\delta^{13}C$ of the TDIC in the anoxic zone. The model predicts that the gases CO_2 and CH_4 are lost to the atmosphere. It is likely that the CH_4 is oxidized in the unsaturated zone and only CO_2 reaches the atmosphere.

Model Limitations

The results from this model are supported by the geochemistry of the anoxic part of the aquifer and examination of the mineral phases. However, the model has certain limitations. The results are based on the input of solid phases that were selected according to the data available, and equally valid models may be obtained by using different phases. This is especially true for the solid solution of $Fe_{.8}Ca_{.2}CO_3$ where the stoichiometry was assigned. The saturation indices calculated with WATEQF indicated that siderite was the phase expected to precipitate. Because siderite was not found in the aquifer, but Fe rich carbonates containing Ca were found, a solid solution was chosen a likely phase to precipitate. Part of the Mg^{2+} that was lost from solution between A and B could have been incorporated into the carbonate solid solution. Such a mineral would have a composition similar to that of a ferroan-calcite, an iron-rich carbonate that contains Fe^{2+}, Ca^{2+}, and Mg^{2+}.

More information about the structures of the clay minerals would improve the model. It is likely that dissolution and reprecipitation of clay minerals could explain the loss of Si and the cations along the flow path. Small amounts of clay minerals of the smectite composition were found in the fine fraction by X-ray diffraction, however, the composition of the minerals is unknown.

The oxidation state of organic material and $\delta^{13}C$ values for the dissolved organic material were assigned rather than measured. The measurements would be difficult to make because the organic carbon in solution is volatile and nonvolatile. In addition, the assumption that carbon can be balanced by measured concentrations of TDOC, CH_4, and TIC is an oversimplification. The reactions that degrade organic material are largely microbial and proceed in several stages. These reactions may produce complex organic compounds that are colloidal or attached to particulate material that are not included in the model.

The assumption was made that no attenuation occurred because of dispersion. A conservative constituent from the oil was not found to estimate dispersion. Because the horizontal distance between the two sites was small, a dispersion factor was omitted. Another assumption was that the ground water at site B had the composition of the water at site A at the beginning of the time a parcel of water was transported from site A to site B. Using a ground-water velocity of 0.06 to 0.14 meters per day, the estimated time of travel between point A and B is 0.8 to 1.8 years. Over that time period, the chemical composition of the plume was stable, however, the $\delta^{13}C$ values of the total inorganic carbon became heavier, which indicates an increasing effect of methanogenesis. In future work, data for aqueous species in ground water will be obtained on a temporal basis to account for the time it takes for a parcel of water to be transported between two sites in the aquifer.

CONCLUSIONS

The effect of hydrocarbons on the geochemistry of an aquifer was investigated by considering the composition of the crude oil, the concentrations of the aqueous chemical species, and the mineralogy of the aquifer. The important chemical reactions in an anoxic zone of the aquifer were determined to explain the changes in water chemistry along a 40-m-long flow path from a point beneath the oil body to a point 40 m downgradient.

Quantitative mass balance and isotope calculations were made using a geochemical mass balance model to determine the mass transfer of phases for the chemical reactions. The results of the model indicate that the major processes are the degradation of hydrocarbons; outgassing of CO_2 and CH_4; dissolution of calcite and iron and manganese oxides; and precipitation of silica and an iron-rich carbonate. In this model the calculated and measured carbon isotopic values are in close agreement with each other. Although the model has limitations and is nonunique, the results are supported by the geochemical data and mineralogic information obtained for the aquifer. Additional data on the isotopic composition of the dissolved organic compounds in the aquifer would remove some uncertainties in the model. Also, structural information about the clay minerals would help explain the loss of Si, K^+, the Mg^{2+} from solution.

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MECHANISMS CONTROLLING THE TRANSPORT OF ORGANIC CHEMICALS IN SUBSURFACE ENVIRONMENTS

By George R. Aiken[1], Paul D. Capel[2], Edward T. Furlong[1], Marc F. Hult[2], *and* Kevin A. Thorn[1]

ABSTRACT

Ground-water contamination by anthropogenic organic chemicals is a significant problem in many areas. In areas of chemical spills, hydrophobic organic compounds have been shown to migrate farther than would be expected on the basis of chemical properties and traditional mass-transport theory. This has been observed for phenanthrene at a site contaminated with crude-oil near Bemidji, Minnesota. A conceptual multiphase model is proposed, which includes equilibrium transport of the chemicals in the vapor phase and in the aqueous phase. Aqueous transport can occur either in the thermodynamically dissolved phase and in association with mobile "particles" (colloids, dissolved organic carbon,dissolved organic carbon-iron complexes, and oil droplets). Stationary particles (the geologic matrix) in the saturated and unsaturated zones attenuate transport by sorption. This conceptual model is used as a framework to discuss past and future investigations of transport of hydrophobic organic chemicals at the study site near Bemidji, Minnesota.

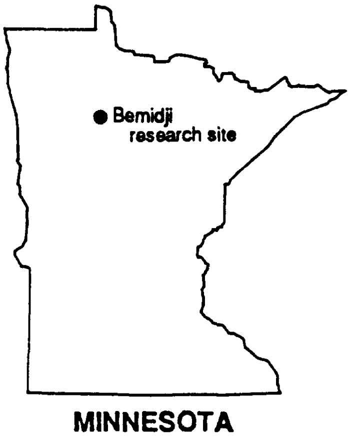

Figure 1. Location of Bemidji research site, Minnesota.

INTRODUCTION

Ground-water contamination by anthropogenic organic chemicals is a significant problem in many areas. Numerous scientific investigations, including a site in Bemidji, Minn. (fig. 1), have been concerned with the fate, transport, and remediation of contaminants introduced into the subsurface through spills. One apparent anomalous result from early research was the apparent migration of hydrophobic chemicals far beyond distances predicted on the basis of chemical properties and traditional mass transport theory. This has been observed for several hydrophobic organic compounds, including polychlorinated dibenzo-p-dioxins (Pereira and others, 1985), hexachlorobenzene (Schwarzenbach and others, 1983), polyaromatic hydrocarbons (Backhus, 1990) and inorganic compounds, including plutonium and americium (Penrose and others, 1990). These findings have led researchers to modify conceptual models of chemical behavior in ground water from simple two-compartment systems (solid/water) to complex multicompartment systems (solids/water/colloids/dissolved organic carbon/organic fluids) (Huling, 1989; McCarthy and Zachara, 1989).

A number of significant, albeit poorly understood, mechanisms can be responsible for the transport of hydrophobic organic chemicals in the subsurface. An organic compound can exist in several chemical environments in an unconfined, contaminated aquifer (fig. 2). In the unsaturated zone, the chemical can exist in the vapor phase or in association with stationary particles (the geologic matrix). In the saturated zone, it can be thermodynamically dissolved in water, dissolved in an organic fluid, in association with stationary particles, or in association with mobile particles. Mobile particles include dissolved organic carbon (DOC), DOC-iron complexes, colloids, and oil droplets. For an organic compound, each chemical state is related to the other states through equilibrium partitioning and air/water exchange. The magnitude of the partitioning coefficients and the abundance of the sorbents determine the mechanisms and velocity of transport of a particular compound in a specific subsurface system.

Application of chromatographic theory to subsurface transport can be of help in understanding and quantifying the chemical processes in subsurface systems. An analogy between chromatography and the movement of organic chemicals in ground water is illustrated in figure 3. Chromatography is virtually the transport of a chemical in a mobile fluid phase (gas or liquid) through a column packed with a stationary phase (an inorganic solid partially covered by organic matter). The chemical is introduced at the head of this column and moves at a rate proportional to the average velocity of the fluid and inversely proportional to the strength and nature of sorptive interactions with the stationary phase. The same framework exists in a ground-water system. The geologic matrix, representing the stationary phase in the analogy, generally consists of sand grains coated with organic matter. In the unsaturated zone, the mobile phase is air. In the saturated zone, the mobile phase is the water, which can contain significant quantities of dissolved organic and inorganic chemicals. An organic compound moves through the subsurface system as a result of the flow rates of air (in the unsaturated zone) and water (in the saturated zone) and the strength and nature of interactions with the stationary phase. In reality, subsurface systems, particularly at a

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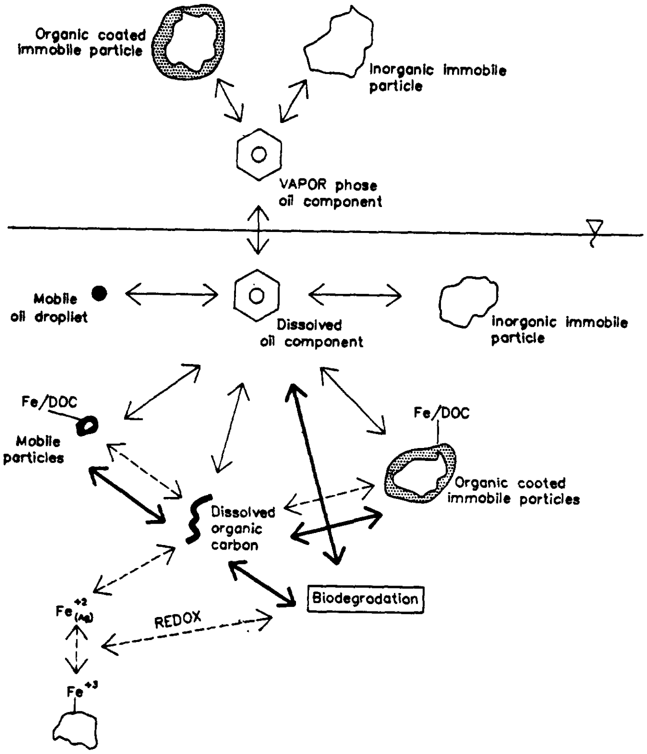
Organic coated immobile particle
Inorganic immobile particle
VAPOR phase oil component
Mobile oil droplet
Dissolved oil component
Inorganic immobile particle
Fe/DOC
Mobile particles
Fe/DOC
Organic coated immobile particles
Dissolved organic carbon
Biodegradation
$Fe^{+2}_{(aq)}$
REDOX
Fe^{+3}

Figure 2. Conceptual model of the equilibrium distribution of a hydrophobic organic chemical component of crude oil, such as benzene, between the various phases in the saturated and unsaturated zones. Superimposed on these distributions are the carbon and iron cycles, which in part, determine the distributions of the hydrophobic organic chemical at any point in time and space.

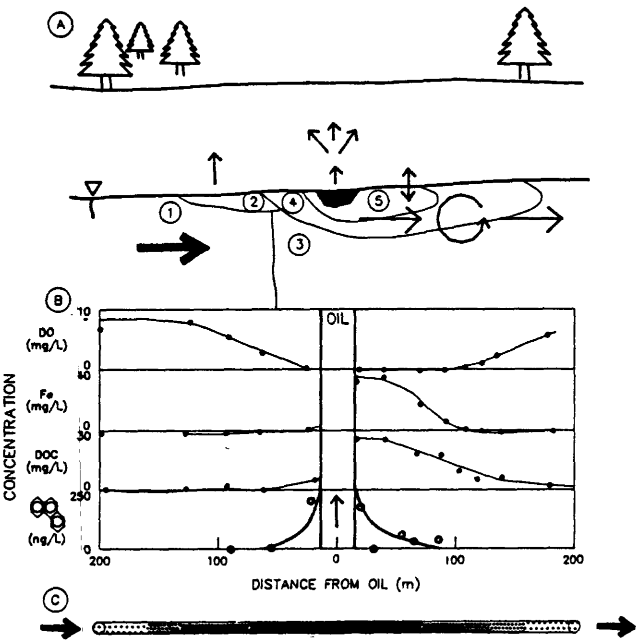

Figure 3. Transport of chemicals at the crude-oil spill site near Bemidji, Minnesota. (A) Schematic of site. The dark arrow represents the direction of ground-water flow. The lighter arrows represent the transport and sorption of hydrophobic organic chemicals. Five zones, based on differences in water chemistry, are delineated. These are described in detail in the text; (B) Concentration of dissolved oxygen (DO), iron (Fe), dissolved organic carbon (DOC), and phenanthrene (⌬) at the water table as a function of distance from the oil body. The horizontal distances are the same in both (A) and (B); (C) Schematic of the analogy between a chromatography column and a contaminated aquifer system. The arrows show the direction of flow. The shading illustrates the changes in the stationary phase surface with distance.

contaminated site, are much more complex than the chromatography column because the composition of both the stationary and mobile phases change as a function of time and space. In an unconfined aquifer, the complexity increases because chemical exchanges occur across the air/water interface, giving rise to an analogy of a gas-chromatographic system continually linked to a liquid-chromatographic system at every point in a two-dimensional plane (the water table).

This paper describes the results of research from the past 5 years conducted at the U.S. Geological Survey (USGS) Toxic Substances Hydrology Program's crude oil spill study site near Bemidji, Minn., that give insight into the transport mechanisms of hydrophobic organic chemicals. Possible areas of future research needed to improve an understanding of the nature and importance of various transport mechanisms of organic chemicals in the subsurface are also identified.

DESCRIPTION OF STUDY SITE AND WATER CHEMISTRY

The USGS crude oil spill study site near Bemidji, Minn., is an excellent site for studying interactions controlling organic compound transport in the subsurface (fig. 4). The aquifer consists of glacial outwash with an irregular surface (Hult, 1987). The aquifer material is well-sorted, medium-grained, sand containing 57 percent quartz, 30 percent feldspar minerals, about 6 percent carbonate minerals, less than 5 percent clay minerals, and less than 2 percent organic carbon (Baedecker and others, 1989). In August 1979, a pipeline carrying crude oil burst, resulting in the contamination of a shallow sand and gravel aquifer (Hult, 1987). After cleanup efforts were completed, approximately 400,000 liters of crude oil remained in the aquifer and overlying unsaturated zone. The resulting 2 to 4 m (meter) thick lens of crude oil is floating on the water table about 8 m below land surface.

In the 11 years since the spill, the crude oil has moved about 30 m downgradient as a separate fluid. Organic constituents have moved at least 200 m in the ground water and about 100 m in the unsaturated zone (Hult, 1989). The crude oil is becoming more viscous, more dense, and more depleted in volatile compounds then the original oil because of selective dissolution and volatilization. Biological degradation of oil components has created an expanding anoxic zone around, immediately under, and downgradient from the oil body. Partial degradation to complete mineralization of the oil have been observed and produced a mixture of dissolved organic compounds downgradient from the oil. Most of these are nonvolatile, yellow-colored, organic acids, which are intermediates in the microbiological degradation

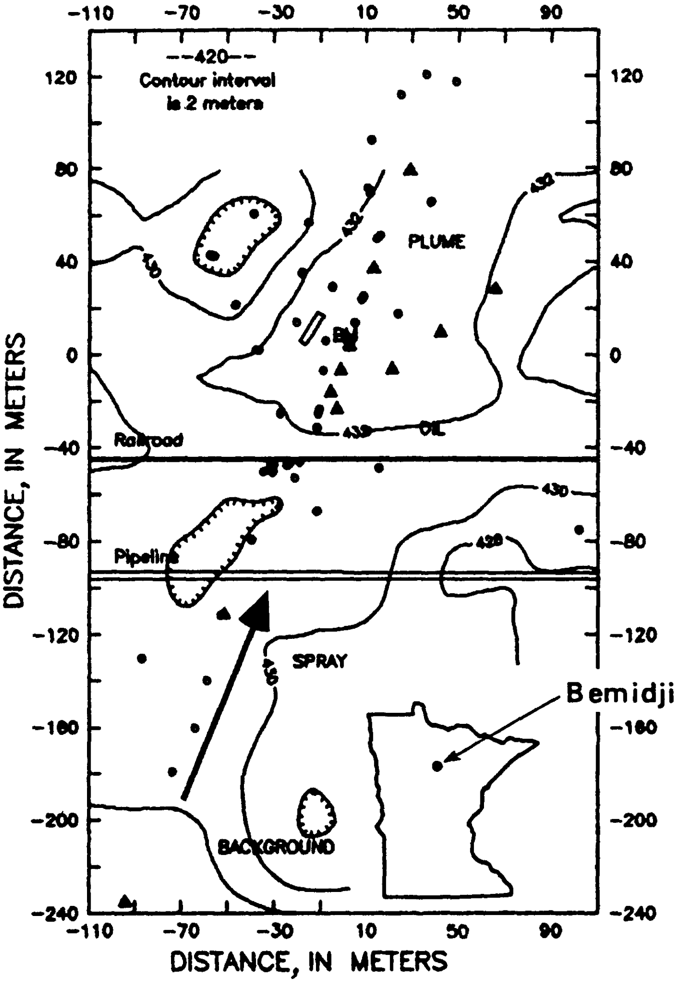

Figure 4. Bemidji research site, Minnesota. Filled circles are piezometers, filled triangles are piezometer nests. Elevations are meters above sea level. Arrow shows approximate direction of ground-water flow (from Bennett, 1988).

of the crude oil (Aiken and Thorn, 1989). In addition, the biodegradation of the crude oil has resulted in the development of distinct oxidation/reduction zones within the plume of contamination downgradient from the oil.

Baedecker and others (1989) have delineated five distinct zones around the oil body on the basis of spatial differences in water chemistry (hydrogen ion, oxygen, bicarbonate, DOC, methane, sulfate, sulfide, nitrate, ammonia, iron, manganese and $\delta^{13}C$). These zones are outlined and numbered in figure 3a. Figure 3b illustrates the spatial changes in the ground-water chemistry on the horizontal same scale as the zones in figure 3a. In each zone, the ground-water chemistry is controlled by different geochemical processes.

The chemical composition of the native ground water, zone 1, is controlled by carbonate equilibrium and, to a lesser extent by mineral dissolution and the degradation of naturally occurring organic matter (Baedecker and others, 1989). The native ground water has a median pH of 7.6, is saturated with dissolved oxygen, and has a DOC concentration of 2 milligrams carbon per liter. This DOC is composed of naturally occurring organic compounds and is predominantly aquatic fulvic acid, differing significantly from the degradation products of the oil in the other zones (Aiken and Thorn, 1989).

The area adjacent to the oil body, zone 5, has the highest concentrations of oil components and oil-derived DOC. Neutral, hydrophobic hydrocarbons are solubilized from the oil body and low molecular-weight organic acids, enriched in aromatic and branched-chained aliphatic components, are created as metabolic intermediates of anaerobic degradation (Cozzarelli and others, 1989). Both the low molecular-weight acids and the hydrocarbons are rapidly attenuated in this zone. Within zone 5, the water is buffered by organic-matter degradation and carbonate and silica mineral-equilibria reactions. The ground water has a median pH of 6.93 and is anoxic. Methane, ammonia, and hydrogen sulfide are generated as dissolved organic compounds are oxidized. Iron and manganese are solubilized because of the reducing conditions. Zone 4 is a transitional region with measurable, but low dissolved oxygen concentrations, increasing pH values, and decreasing concentrations of iron and DOC. In zone 3, the water chemistry returns to oxidizing conditions, but evidence of the contamination plume from the oil can still be observed. This zone still has higher-than- background concentrations of most constituents and trace concentrations of oil hydrocarbons are present. The discussion in this paper focuses on zones 3, 4, and 5.

DISCUSSION

Vapor-Phase Transport

Vapor-phase transport and its relation to ground-water transport has not been considered previously in conceptual transport models of hydrophobic organic compounds in unconfined aquifers. At the Bemidji site, hydrophobic organic chemicals can migrate into the unsaturated zone by at least three routes: volatilize from the oil body, undergo air/water exchange at the water table, and volatilize from oil coated sand grains remaining after fluctuations of the water table (figs. 2 and 3). Once in the unsaturated zone, organic chemicals can be transported in the vapor phase by advection and diffusion. The chemical may ultimately be transformed, lost to the atmosphere from the soil, or reenter the ground water. Therefore, a molecule observed in water downgradient from the oil body may have arrived there through vapor transport and not aqueous transport. Past work in the unsaturated zone at the Bemidji site has documented the presence of C_1 to C_8 saturated and C_6 to C_9 aromatic hydrocarbons (Hult; 1987; 1989). Some of these chemicals have been shown to be transported farther than 100 m through the unsaturated zone by diffusive and advective (biologically induced convection) mechanisms. Further evidence is needed to determine the importance of this vapor-phase movement and subsequent air/water exchange on the "apparent" transport of hydrophobic compounds in ground water. In our chromatography analogy, the vapor phase represents a dynamic, three-dimensional gas-chromatographic system linked to a liquid-chromatographic system in time and space.

Solid-Phase Interactions

The role of the stationary particles (geologic matrix), whether in the unsaturated or saturated zone, is attenuation of hydrophobic chemical transport through sorption processes. All of the stationary-particle surfaces, especially near the site of contamination are covered with an organic coating (DOC, oil components, or both), which changes character in space and time. Sorptive interactions between the DOC and stationary particles removes the DOC from solution and changes the surface of the particles (fig. 2). This process is a function of the chemical properties of the DOC, the particle-size distribution, and the chemistry of the ground water. Most of the oil-derived DOC compounds at the Bemidji site are relatively hydrophobic compared to the naturally occurring DOC (predominately fulvic acids) in the ground water. The oil-derived DOC can interact directly with mineral surfaces, with the naturally occurring organic matter previously sorbed onto the stationary particles, or as organic-iron complexes. Although little is known about the nature of these solid-phase organic coatings, it is important to recognize that the organic coatings on the stationary particles materials have a profound effect on their sorptive properties for hydrophobic organic chemicals. In our chromatography analogy, the sorptive removal of the DOC by the geologic matrix results in changes in the stationary and mobile phases in time and space.

Aqueous-Phase Interactions

Transport in the saturated zone can only occur when chemicals are in the water. Hydrophobic organic chemicals can exist in ground water contaminated with an organic fluid in a number of chemical states, including being thermodynamically dissolved or associated with mobile "particles" such as oil droplets, colloids, DOC, and DOC-iron complexes. Transport of hydrophobic chemicals in association with mobile "particles" has been termed "facilitated transport" (Huling, 1989).

Field evidence at the Bemidji site suggests that the presence of phenanthrene 80 m downgradient from the oil results from facilitated transport (fig. 3b). In this system, phenanthrene, with a log K_{ow} of 4.6, would not be expected to move this far downgradient in the thermodynamically dissolved state. The three polycyclic aromatic hydrocarbons present in the crude oil (naphthalene, fluorene, and phenanthrene) are routinely identified in ground-water samples downgradient from the oil body, but no other polyaromatic hydrocarbons of higher molecular weight were observed in either the water or the crude oil isolated from this site.

To date, the research at the Bemidji site, which provides information related to facilitated transport processes, is the characterization and transport of DOC and its interactions with dissolved and precipitating iron. The DOC is a highly complex and transient mixture. The individual organic compounds comprising this mixture differ with respect to aqueous solubility, chemical stability and reactivity, and biodegradability. The presence of certain DOC constituents is strongly dependent on the oxidation/reduction state of the ground water, which controls the types and rates of biodegradation processes. Increases in chemical hydrophobicity, aromaticity, and molecular weight and size of the DOC enhance facilitated transport by increasing the strength of the DOC-hydrophobic chemical interactions. Results of elemental analyses and molecular-weight determinations indicate that the oil-derived DOC consists of hydrophobic acids, which contain a greater percentage of carbon and hydrogen and a lower percentage of oxygen and nitrogen than the naturally occurring DOC (Aiken and Thorn, 1989). In addition, ^{13}C-nuclear magnetic-resonance analyses indicate that the oil-derived DOC contains a large amount of aromatic carbon (19 percent). Although the number-average molecular weights of the hydrophobic acids from the contaminated wells are relatively low compared to that of the natural DOC, equilibrium dialysis experiments have shown that greater than 10 percent of oil-derived DOC is large enough to be retained in the 2,000 to 12,000 molecular-weight size fraction. Altogether, these results suggest that the DOC is potentially capable of interacting with hydrophobic organic compounds and facilitating their transport in the aquifer.

The interactions between the DOC and iron in the anoxic zones of the plume and oxidation/reduction interface, where the iron is precipitating, can affect the sorption and transport of hydrophobic organic compounds. Interactions between organic matter and iron have been noted in soils (Senesi, 1981; Antweiler and Drever, 1983), in fresh surface waters (Sholkovitz and Copland, 1981) and in anoxic sediments (Krom and Sholkovitz, 1978). In addition, Krom and Sholkovitz (1978) and Sholkovitz and Copland (1981) have demonstrated that interactions between organic matter and iron are stronger than the interactions between organic matter and other transition metals of environmental and geochemical significance. At the Bemidji site, the occurrence of organic acid- iron interactions has been demonstrated. Berndt (1987) has observed that 25 to 48 percent of iron extracted from aquifer materials downgradient of the oil body are associated with organic matter. Also, calculations of apparent solubility for iron suggest that it is supersaturated with respect to thermodynamically predicted iron-mineral species throughout zone 5. Finally, preliminary results from fluorescence-quenching measurements of ground water sampled from a transect of the major plume axis (fig. 4) suggest a significant interaction between DOC and iron, and perhaps, between DOC and hydrophobic organic chemicals.

The transient, chemical composition of the aqueous phase and its interactions with hydrophobic organic compounds suggest that concurrent, diverse transport mechanisms are at work in contaminated ground water. Understanding the role of DOC and DOC-iron complexes on hydrophobic chemical transport is beginning, but the abundance and nature of other "mobile particles" (colloids, oil droplets) have not yet been explored at the Bemidji site.

SUMMARY

The transport of hydrophobic organic compounds in ground water has been shown, in numerous investigations, to exceed the distances predicted by chemical properties and traditional mass-transport theory. In order to explain their movement, nontraditional transport mechanisms are suggested for the hydrophobic compounds, including transport in the aqueous phase in association with mobile "particles" (colloids, oil droplets, DOC, DOC-iron complexes) and transport in the vapor phase. Altogether, transport of a chemical in association with mobile "particles" has been termed facilitated transport. Results of research at a USGS study site in Bemidji, Minn., has demonstrated transport of organic chemicals in both the vapor and aqueous phases. Preliminary evidence supports facilitated transport for phenanthrene. Data regarding DOC and DOC-iron complexes suggest that they may participate in the facilitated transport of hydrophobic organic chemicals. Although some information has been derived from studies at this site, many open questions still exist concerning the transport of hydrophobic organic chemicals in the subsurface.

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THE CHEMISTRY OF SILICA-ORGANIC COMPLEXATION IN A PETROLEUM-CONTAMINATED AQUIFER

By Philip C. Bennett[1]

ABSTRACT

Organic substances generated by microbial activity in a petroleum contaminated sand and gravel aquifer accelerate the rate of silicate dissolution and increase the solubility of quartz. Experimental investigations of quartz dissolution experiments show that some simple organic acid-anions accelerate quartz dissolution at circum-neutral pH below 70 degrees Celsius. These observations suggest that silica is complexed by organic substances both in solution and at the quartz-water interface. Molecular orbital modeling of potential complex-structures suggests that a critical factor is the O-Si-O bond angle. Modeling of solution complexes offers insight into the mechanism of dissolution rate enhancement by suggesting possible surface-activated complexes.

INTRODUCTION

The unusual mobility of silica in some organic-rich natural waters has challenged researchers to propose new mechanisms of quartz dissolution that incorporate silica/organic complexes. Although the existence of an interaction between dissolved organic compounds and silica has been hypothesized for more than 100 years (for example, Julien, 1879), direct evidence supporting the presence of a silica/organic complex in natural waters has been elusive.

Evidence that some organic compounds chemically weather quartz in petroleum-contaminated ground water was previously reported by the author (Bennett and Siegel, 1987). It was found that in the most highly contaminated region at the research site in Bemidji, Minn. (fig. 1), the concentration of dissolved organic carbon was correlated with the concentration of dissolved silica. Little silicon was found in the crude petroleum, indicating an inorganic solid-phase source of dissolved silica. Investigations using scanning electron microscopy showed that quartz and aluminosilicate sand grains collected from the contaminated zone of the aquifer were being chemically weathered at an accelerated rate. However, the ground-water pH in that zone was 6.4 to 6.8, and the water was greatly supersaturated with respect to quartz and in approximate equilibrium with amorphous silica. The zone of greatest silica mobility occurred where the concentration of soluble hydrophobic organic acids is greatest (Aiken and others, 1989), and where the oxidation potential of the water is lowest (Baedecker and others, 1989). In this geochemical zone, silica is mobilized coincidentally with iron and manganese (Bennett, 1991). Farther downgradient, both iron and silica rapidly precipitate together where the ground water becomes more oxidizing because of the increased availability of dissolved oxygen from diffusion and mixing of uncontaminated waters.

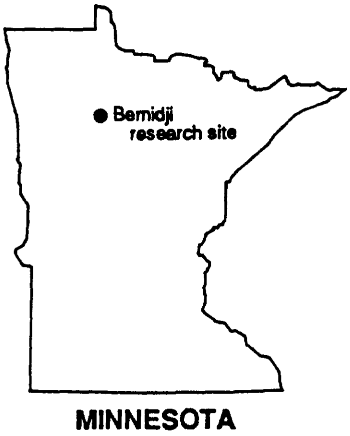

Figure 1. Location of Bemidji research site, Minnesota.

The observations made at the Bemidji site suggest that the interaction between silica and dissolved organic acids is significant, and that this interaction is a factor in sediment diagenesis in that environment. To investigate the nature of this interaction, electronic and vibrational spectroscopy and batch reactor dissolution experiments were designed to (1) identify the nature of the silica/organic association in solution, and (2) determine the influence of organic substances on the kinetics of dissolution and on the equilibrium solubility of quartz in water. The results of these experiments were further evaluated using molecular orbital modeling techniques to examine vibrational, electronic, and structural characteristics of the hypothetical aqueous and surface complex.

DISSOLUTION EXPERIMENTS

The kinetics of quartz dissolution in simple inorganic and mixed inorganic-organic electrolyte solutions was examined using a batch-reactor system at temperatures ranging from 25 to 70 °C (degrees Celsius). Solution composition, concentration, and pH were varied in order to investigate their effects on the dissolution rate and the steady-state solubility of quartz.

The effect of solution pH and alkali ion concentration on the dissolution of quartz were investigated first to determine that contribution to the results of the mixed electrolyte dissolution experiments. The dissolution rate of quartz decreased slightly with a decrease in pH from pH 7 to 3, similar to the results of Knauss and Wolery (1988). Preliminary results indicate, however, that the dissolution rate may increase from pH 3 to 1.1. The effect of dilute solutions of alkali chloride salts (<10 mml (millimolal)) was found to increase slightly the rate of quartz dissolution at 25 °C. Dissolution rate increased with increasing alkali chloride salt concentration between 10 and 100 mml, yielding a reaction order of approximately 1. The rate enhancement was greatest in solutions of cesium chloride, and least in lithium chloride, with constant chloride concentration, suggesting an interaction between the alkali metal and the quartz surface. Furthermore, the significance of salt enhancement appears to increase with increasing temperature (Dove and Crerar, 1990).

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The rate of quartz dissolution in inorganic electrolyte solutions at pH 7 increased as a function of temperature in a manner similar to results reported by Rimstidt and Barnes (1980). In the study described here, the rate of dissolution at 40 °C was about $10^{-16.55}$ mol/cm^2/s (moles per square centimeter per second) in pure water, and was $10^{-15.12}$ mol/cm^2/s in a 50 mml KCl in a K-phosphate buffer solution. At pH 4.5, however, there was no significant difference between the rate in distilled water, and the rate in 50 mml inorganic electrolyte solutions. Evaluation of the relation between rate constant and temperature yields a calculated activation energy of 17.2 kcal/mol (kilocalorie per mole) for the simple inorganic system, within the range of 16 to 18 kcal/mol reported by Rimstidt and Barnes (1980). Where steady-state was attained, the final concentration of H_4SiO_4 was close to that predicted by Fournier and Potter (1982).

In contrast, the dissolution of quartz in potassium citrate solutions at pH 7 was significantly faster than the rate measured in an equimolar solution of inorganic salts, and yielded a calculated activation energy of 14.6 kcal/mol. The relative difference in rate was approximately 0.6 log rate units at 25 °C, and decreased to less than 0.1 log rate units at 70 °C. Similar results were obtained with potassium oxalate. In addition, dissolution rate increased with increasing concentrations of both citrate and oxalate salt solutions. Other organic acids, such as acetic and benzoic acids, had no apparent effect on the dissolution of quartz at temperatures above ambient.

SPECTROSCOPY

Preliminary experiments to examine the nature of the silica/organic association used Ultraviolet (UV) -difference spectroscopy (Bennett and others, 1988). This technique examines the electronic absorption characteristics of the individual components of a mixture and compares that to the mixed system. These experiments suggested that monomeric silicic acid forms an aqueous complex, possibly in the form of an electron donor-acceptor complex (Gutmann, 1978), with certain multifunctional organic acid at near-neutral pH. This complex is not stable at acidic pH, and was not found with monofunctional organic acids. These results support the hypothesis that silica is complexed by organic acids, but ambiguities remained due to inherent experimental artifact.

Additional experiments were undertaken, using Raman and Fourier transform infrared (FTIR) spectroscopy, to examine the nature of the complex directly. Using the difference technique, a silica/organic complex was tentatively identified by FTIR and Raman experiments Marley and others (1989). They suggested that the nature of the interaction at higher concentrations may be as a silica/organic ester, but these results have been difficult to reproduce and may be due to experimental artifact.

DISCUSSION

UV absorption spectroscopy suggests that some multifunctional organic acid anions at low concentration interact with dissolved monomeric silicic acid at circum-neutral pH by way of a charge-transfer complex. The interaction is pH-and concentration-dependent (Bennett and others, 1988). Molecular models show that both a bidentate hydrogen bonded and a bidentate siloxane bonded structures are possible in aqueous systems; a pentacoordinate silicon-organic transition state complex is intermediate between the two structures. A possible initial reaction sequence for the silica-oxalate reaction is

$$Si(OH)_4 + C_2O_2= \text{-->} \ (OH)_3Si : C_2O_2^- + OH^-, \quad (1)$$

where the hydrogen bonded complex first forms a monodentate siloxane chelate, accompanied by a hydrogen bond to the other oxalate oxygen functionality, and a hydroxyl ion as a product. Based on the results of the modeling studies, this reaction is hypothesized to continue, forming a bidentate siloxane chelate in a ring-structure.

The dissolution experiments support the hypothesis of a silica/organic solution complex. Some multifunctional organic acid anions, such as citrate and oxalate, enhance the dissolution of quartz in aqueous solutions. The rate of dissolution increases with increasing concentration. Also, the solubility of silica in organic-acid-anion solutions is greater than the solubility of the equimolar salt solution and the predicted equilibrium solubility. Other acid anions, such as acetate, show no significant interaction or actually decrease the dissolution rate. It was also found that organic acid-anions in solution increase the rate of dissolution of quartz, even at small reaction extents, and decrease the activation energy of dissolution. This would suggest that the organic anions form an activated surface complex that is favorable to the dissolution of quartz. The order of organic acid reactivity for both rate and solubility enhancement was

citrate > oxalate >> salicylate ≥ phthalate.

This order of reactivity suggests that bidentate complexes forming a ring structure are more effective than monodentate linear structures, and that the smaller ring is a more stable structure. When the results of the spectroscopy and dissolution experiments are factored into the modeling studies, complexes forming five-member rings are found to be the most stable, with stability decreasing with increasing ring size. This is similar to the results of (Stumm and Furrer, 1987) for aluminum-organic complexes. The geometry of the complex is particularly important, as a five-member ring results in unacceptable angle strain if normal bond angles are assumed. The molecular orbital modeling suggests, however, that the normal bonding sp^3 orbitals are polarized by low-lying d-orbitals, resulting in a O-Si-O bond angle of 93°, rather than the expected 109° tetrahedral bonding environment, markedly decreasing the bonding angle strain. This geometry is actually found to be common with organosilicon compounds, including the catechol-silica complex previously identified in aqueous systems (Iler, 1979). Citrate probably forms a tridentate complex.

From these relations a model of interaction for silica/organic solution complexes can be hypothesized. A "fast" initial solution complex might form a low-energy hydrogen-bonded complex. A slower, less favorable reaction could be the formation of a silica/organic ester. These reactions would decrease the activity of monomeric silicic acid, thereby increasing the solubility of quartz. Based on the structure of the solution complex, several reactions can be hypothesized to occur on the silicate surface. One possibility is the documented destabilization of framework Si-O bonds due to the interaction of a surface bound electron donor (Gutmann, 1978). This could result in the observed rate increase accompanied by a decrease in the activation energy of dissolution. Another possibility is linked to bonding-orbital polarization postulated for the solution complex. If an inner-sphere complex of citrate on a quartz surface results in a change in bonding environment of the surface silicon atoms, this may decrease the steric hindrance of nucleophilic hydrolysis by water, thus increasing the rate of dissolution. This is similar to the mechanism of alkali metal catalysis of quartz dissolution hypothesized by Dove and Crerar (1990).

CONCLUSIONS

These results suggest that the presence of high concentrations of dissolved organic acids accelerates the dissolution of quartz and aluminosilicate minerals, even at near-neutral pH where aluminum complexation is less significant. This is accompanied by an increase in the apparent solubility of quartz in water, because of the decrease in the activity of monomeric silicic acid. The mobility of silica is greatest in reducing waters, possibly due to the presence of keto- and hydroxy-acids that may not be stable in oxidizing waters. The labile nature of the complex suggests that the complex may disassociate when conditions of pH or Eh change.

This reaction mechanism may act as a significant diagenetic force in some organic-rich sediment environments. Porosity may increase in regions of high organic acid content and reducing conditions, and decrease where pH or Eh conditions change. Solubilization of silica at neutral pH might also offer a mechanism for silicate dissolution with aluminum conserved in a solid phase. Research is continuing into the structure and reactivity of the silica/organic complex using spectroscopy and molecular orbital modeling, and into microbial controls on organic acid generation.

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EVOLUTION OF PHYSICAL PROPERTIES AND COMPOSITION OF A CRUDE OIL SPILL

By Matthew K. Landon[1] *and* Marc F. Hult[1]

ABSTRACT

The spatial distribution and characteristics of crude oil spilled August 20, 1979, have been monitored since 1983 at the Bemidji, Minnesota, research site. Oil has migrated at least 30 meters as a separate fluid phase in a glacial-outwash aquifer and is losing soluble and volatile compounds through dissolution into ground water and vaporization into the unsaturated zone. Spatial differences in the physical properties and composition of the oil have developed owing to alteration of the originally uniform source. Gas-chromatographic headspace analysis shows that the oil is selectively losing compounds with low molecular weights, mainly alkanes, through volatilization. Oil samples subjected to volatilization under controlled conditions in the laboratory show systematic relations among viscosity, specific gravity, vapor pressure, refractive index, and composition similar to those exhibited by field samples. Observed changes in physical properties of crude oil at the site reflect yearly oil-mass loss rates ranging from 0 to 1.25 percent (average 0.5 percent) and total losses from the original oil mass as high as 11 percent (average 3.8 percent). Temporal and spatial variations in the physical properties and composition of crude oil at the Bemidji site from 1984 to 1989 are not uniform and indicate that alteration rates are highly variable. The refractive index of oil can be used as a surrogate measure of mass loss and composition using samples as small as a single drop, thereby permitting mass loss to be calculated for oil droplets from cores. This work provides a method of quantifying rates of loss from the crude oil source, a critical step in calibrating transport models of volatile and soluble constituents.

INTRODUCTION

The chemical and physical properties of crude oil in a shallow subsurface environment are subject to alteration as a result of loss of volatile compounds through vaporization into the unsaturated zone, leaching of soluble compounds through dissolution into ground water, and biodegradation. These changes can affect the movement and potency of an immiscible petroleum pool as a source of environmental contamination.

This paper presents the results of ongoing research at the research site in Bemidji, Minn. (fig. 1), on changes in the characteristics of an immiscible crude-oil pool in the shallow subsurface occurring as a result of natural alteration. The objectives of this paper are to describe temporal and spatial variations in physical properties and composition of oil at the Bemidji site and estimate losses of mass from the immiscible crude oil source body. The 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, 1984). A description of site characteristics is given by Hult (1984).

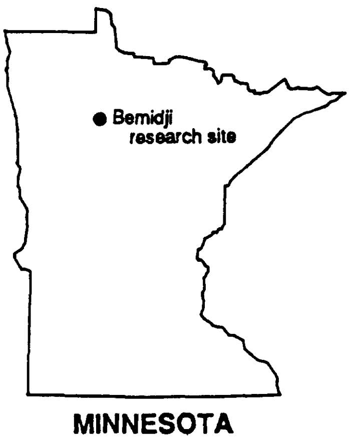

Figure 1. Location of Bemidji research site, Minnesota.

METHODS

One-liter oil samples were bailed from shallow ground water monitoring wells at the Bemidji site in the summer of 1985, June 1988, and July 1989, immediately sealed in airtight containers to prevent loss of volatiles, and shipped to the laboratory for cold storage. The viscosity and specific gravity of the oil samples were measured using standard ASTM procedures. Refractive index was measured with an Abbe-type refractometer. Vapor pressure was measured using water manometers. Oil samples collected in the field were also subjected to volatilization in an environmental chamber held at the Bemidji site average ground water temperature 7.5 °C (degrees Celsius) in order to determine the relations among the physical properties and mass loss. Air was forced through the chamber at 12 cubic feet per hour. This flow rate is low enough to prevent accelerated flushing of volatiles from the oil surface but is sufficient to prevent a static oil-gas phase equilibrium condition from developing in the enclosed 6-cubic-foot chamber. Gas chromatographic headspace analysis was used to measure the composition of the volatile fraction of crude oil at the Bemidji site.

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RESULTS

Physical Properties of Field Samples

Significant variations in the kinematic viscosity and specific gravity exist in crude oil at the Bemidji site (fig. 2). The variations in kinematic viscosity and specific gravity follow systematic trends, which suggest that systematic alteration of crude oil is taking place. Similar trends exist for refractive index, vapor pressure, and composition. There are strong correlations among viscosity, specific gravity, refractive index, vapor pressure, and composition of the volatile fraction of the crude oil, indicating that all of these characteristics are sensitive to the degree of oil alteration. Oil viscosity ranges from 10 to 25 10^{-6} square meters per second, specific gravity from 0.85 to 0.87, and refractive index from 1.480 to 1.489.

Changes in viscosity and specific gravity from 1988 to 1989 are shown in figure 3. Although viscosity and specific gravity of Bemidji oil generally increased from 1988 to 1989, the rate of change in the physical properties was highly variable for oil from different locations in the oil pool (fig. 3). The rates of alteration of physical properties changes through time as well. Alteration rates from 1985 to 1988 are different than those from 1988 to 1989.

Composition of Field Samples

The crude oil at the Bemidji site consists predominantly of light aliphatic compounds (Baedecker and others, 1984). Gas-chromatographic headspace analysis shows that the oil is selectively losing compounds with low molecular weights, mainly alkanes, through volatilization. The concentration of C4-C7 alkanes, benzene, and toluene relative to that of octane for different oil samples at the Bemidji site are shown in figure 4. Compounds with molecular weights lighter than C7 are distinctly depleted in the most weathered samples relative to the least altered samples. Ratios of C7 to C8 are relatively unchanged, suggesting that C7 and C8 are only slightly depleted in the more weathered oil. Ratios of benzene and toluene to C8 are also similar except for the most weathered oil (sample 309, fig. 4).

Physical Properties of Laboratory Samples

Changes in the viscosity and specific gravity of Bemidji oil samples subjected to volatilization under controlled conditions in the laboratory are shown in figure 5. Changes in the physical properties of oil subjected to laboratory conditions (fig. 5) closely match the systematic trends exhibited by oil samples collected from the field (figs. 2 and 3). This result strongly suggests that the variations in the physical properties and composition of the oil have developed from alteration of an originally uniform source and that spatial variations are the result of a nonuniform rate of oil alteration in different areas of the spill. The similarity of variations in physical properties observed in the field and in the laboratory, as well as the observed selective depletion of volatile compounds, suggests that most of the mass loss from the oil results from volatilization. This theory is reasonable given that the oil consists predominantly of light aliphatic compounds that are more likely to partition to the gas phase than to the aqueous phase. However, the exact contribution of other mechanisms, such as biodegradation and dissolution of soluble compounds into ground water, are as yet unknown and undoubtedly affect the results to some degree.

Calculation of Mass Losses

The observed changes in physical properties can be used to estimate the percentage of and yearly rates of mass loss from the Bemidji oil source. The relation of the fraction of total mass lost to specific gravity, viscosity, and refractive index was determined from the laboratory measurements. A strong linear relation between changes in specific gravity and mass loss throughout the range of observed specific gravity values is shown in figure 6. A similar linear relation is evident for mass loss as a function of refractive index (fig. 7). The relation of viscosity and mass loss is nonlinear but may still be used to make mass-loss calculations.

The percentage of mass lost from original oil can be estimated from differences in physical properties of the altered oil relative to the properties of the least-altered field sample of oil. Calculated values of total mass loss are estimates of the minimum amount of mass loss that has occurred from oil of original composition. These estimates are based on the assumption that the currently least altered oil has the same physical attributes as the oil of original composition. However, some alteration of the least modified crude oil has likely occurred. The mass loss required to account for the observed physical properties of oil samples collected in 1989 is shown in figure 8. The percentage of mass removed from oil at a particular location was calculated using changes in density and viscosity relative to the least altered oil sampled in 1988. The measured changes in physical properties reflect total losses from the original oil as high as 11.0 percent and average losses of 3.8 percent. Over the 10-year period from the summer of 1979 to the summer of 1989, this represents an average annual loss of 0.4 percent, although the rate of mass loss is expected to be nonlinear as the more volatile compounds are selectively removed from the crude oil.

Annual rates of mass loss from oil can be calculated from the change in viscosity or density of oil over time. Calculated rates of annual mass loss using yearly changes in physical properties are more speculative than total mass-loss calculations because, as shown in figure 3, changes in physical properties of oil from individual wells from 1988 to 1989 do not, in all cases, have the same slope as the measured general alteration trend or the alteration trends from the laboratory experiments. For most of the samples, there is either an increase in viscosity and specific gravity, the slope of which is close to the slope observed in the lab, or there is no change. Yearly mass-loss rates ranged from 0.1 to 1.25 percent, with an average value of about 0.5 percent for 1988-89. This value is slightly higher than the average yearly loss rate of 0.4 percent determined from the mimimum total-loss calculations.

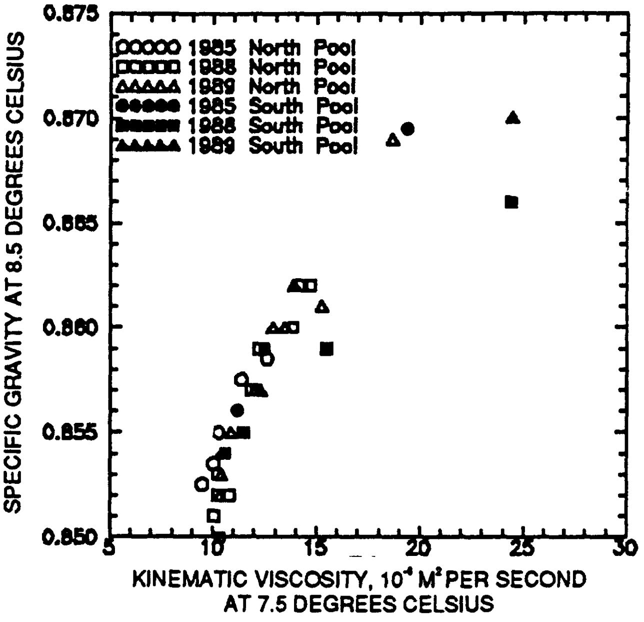

Figure 2. Relation of kinematic viscosity to specific gravity of Bemidji crude oil collected from monitoring wells in 1985, 1988, and 1989.

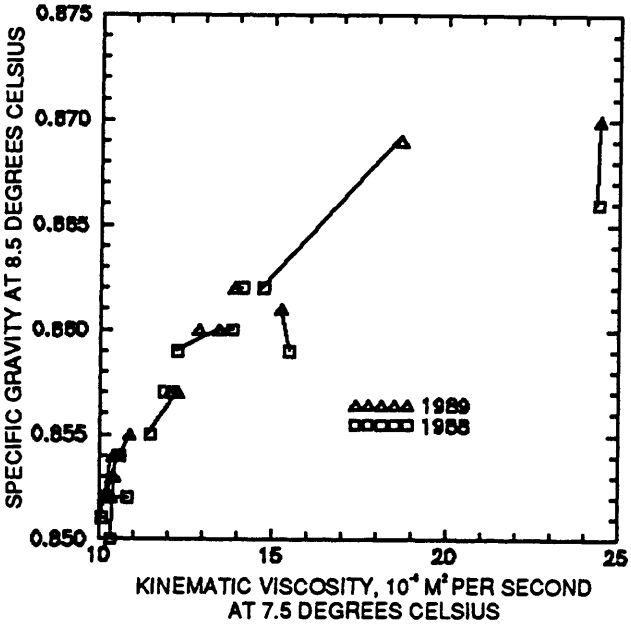

Figure 3. Relation of kinematic viscosity to specific gravity of Bemidji crude oil collected from monitoring wells in July 1988 and June 1989. Lines connecting data points indicate the change in the viscosity and specific gravity of oil from a particular well between 1988 and 1989.

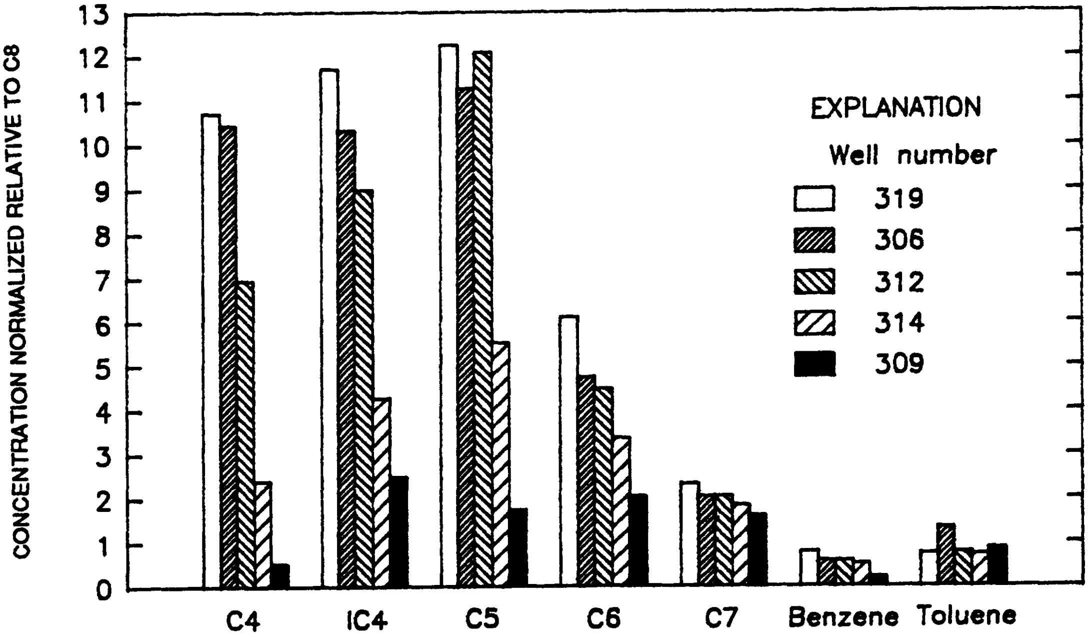

Figure 4. Normalized concentration of selected C4-C7 alkanes, benzene, and toluene in headspace of samples of Bemidji crude oil. Concentrations are normalized to headspace concentration of C8. Numbers corresponding to bar graph patterns refer to well numbers at the Bemidji site from which oil samples were collected. (Chemical compound key: IC4=iso-butane, C4=butane, C5=pentane, C6=hexane, C7=heptane).

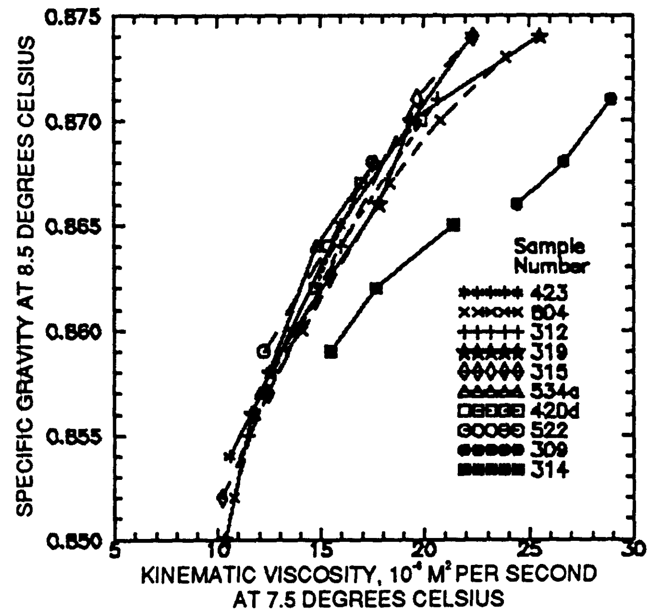

Figure 5. Changes in kinematic viscosity and specific gravity of Bemidji crude oil samples subjected to volatilization under controlled laboratory aging experiments. Lines connecting data points show the change in kinematic viscosity and specific gravity for a particular sample over the course of the aging experiment.

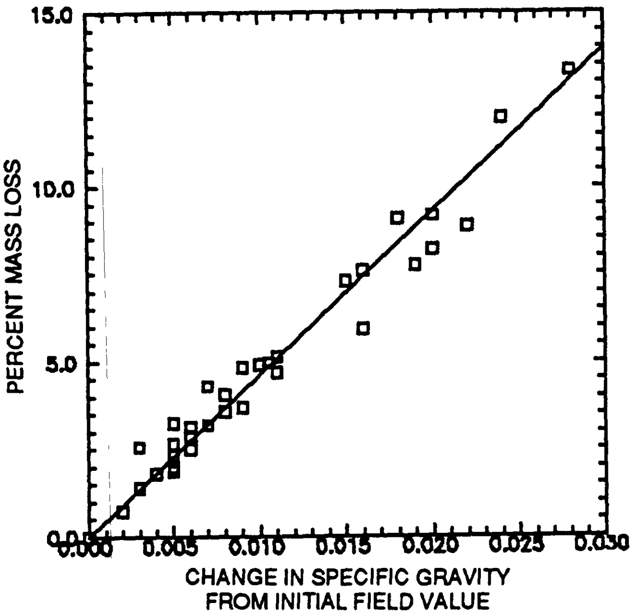

Figure 6. Relation of change in specific gravity from initial field value to percent mass loss for oil subjected to volatilization under controlled laboratory aging experiments. The linear regression indicates that a change in specific gravity of 0.001 results from a mass loss of 0.45 percent.

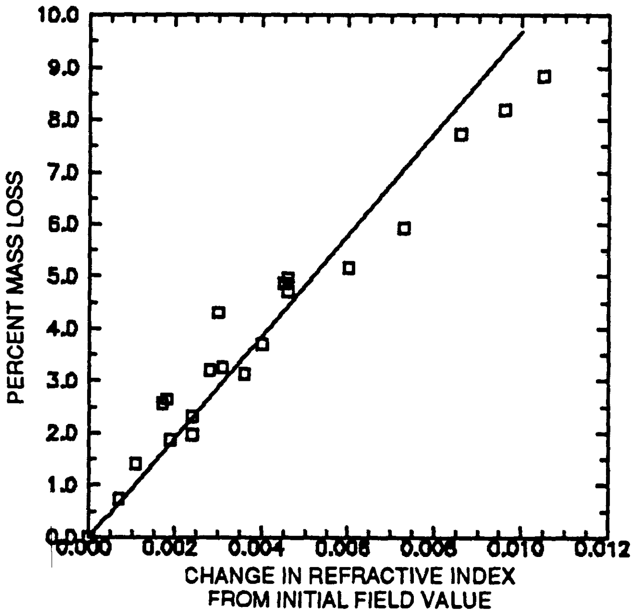

Figure 7. Relation of change in refractive index from initial field values to percentage mass loss for oil subjected to volatilization under controlled laboratory aging experiments. The linear regression indicates that a change in refractive index of 0.001 results from a mass loss of 0.97 percent.

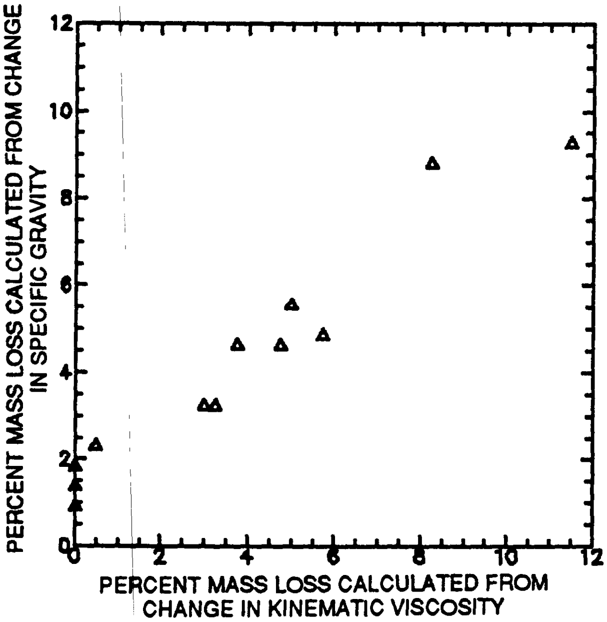

Figure 8. Percentage mass loss from oil of original spilled composition estimated from kinematic viscosity and specific gravity of oil collected in 1989.

CONCLUSION

Systematic alteration of the physical properties and composition of an originally uniform crude oil has occurred as a result of losses of volatile compounds from crude oil in the shallow subsurface at the Bemidji site. Spatial and temporal variations in physical properties and composition of the immiscible crude oil are manifested in measurements of oil viscosity, specific gravity, refractive index, vapor pressure, and composition. Kinematic viscosity has increased by as much as 250 percent, whereas the maximum change in specific gravity is only 2.4 percent. Changes in the characteristics of the oil occur by volatilization of low molecular weight compounds, mainly alkanes, from the oil. Physical properties of Bemidji oil samples subjected to volatilization under controlled laboratory conditions closely match systematic trends in physical properties for oil collected in the field, permitting computation of mass loss from the oil source. Estimates of minimum total losses of mass from different parts of the spill range from 0 to 10 percent but average about 4.0 percent. This total loss corresponds to an average loss of 0.4 percent per year for 1979-88. Rates of annual mass loss, calculated from changes in oil viscosity and density at specific well locations range from 0 to 1.25 percent and average about 0.5 percent. Measurements of refractive index can be performed very quickly, require only a single drop of oil and can be used to measure the bulk composition and degree of alteration of subsamples collected from cores through the immiscible petroleum source. These measurements would permit microscale characterization of source properties and alteration processes on a scale previously unobtainable in the field. Results of this study provide an independent estimate of the areally variable source term for transport models of volatile and soluble constituents and will be used to calibrate such models to field data.

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KINETICS OF CRUDE-OIL BIODEGRADATION BY BACTERIA INDIGENOUS TO SEDIMENT AND GROUND WATER

By Fu-Hsian Chang[1], Hai Wang[2], Brenda Denzin[1], *and* Julie Buller[1]

ABSTRACT

In this study, static and microcosm systems were used to conduct biodegradation experiments of crude oil by indigenous microorganisms over a period of 6 months. Kinetic models were developed to predict rates of biodegradation of crude oil in ground-water environments. The Monod equation was applied to describe the rate of substrate consumption by indigenous crude-oil-degrading bacteria grown in static or microcosm systems. A variety of environmental factors were examined to determine their effect on biodegradation kinetics of crude oil: the concentration of crude oil, redox potential (or dissolved-oxygen), availability of inorganic nutrients (such as nitrogen and phosphorus), population density of crude-oil-degrading bacteria, and temperature of the environment. In order to simplify the kinetic study, temperature was treated as an independent variable and the other five parameters were treated as interdependent. Five differential equations were proposed to describe their interrelations. The equations were solved by the fourth-order Runge-Kutta numerical method. The maximum specific growth rate and turnover time were 0.092 to 0.291 per hour and 1.57 to 4.35 days, respectively, in samples treated with 200 milligrams per liter of crude oil; and 0.051 to 0.207 per hour and 1.72 to 4.49 days, respectively, in samples treated with 400 milligrams per liter of crude oil. Yield coefficients, which increased with increasing temperature, ranged from 0.12 to 0.41 and 0.14 to 0.47 for samples treated with 200 and 400 milligrams per liter of crude oil, respectively. Both maximum specific growth rate and rate constant for the disappearance of the substrate (Ks, in micrograms per liter) increased with rising incubation temperature and increasing substrate concentrations. The maximum biodegradation rate ranged from 5.93 to 17.39 micrograms per milliliter per hour, whereas the rate constant (K_t) varied from 0.51 to 0.99 micrograms per milliliter. Both maximum biodegradation rate and Kt increased with incubation temperature. This study indicated that the biodegradation rate conformed to fourth-order kinetics, which may be as appropriate as second-order kinetics for biodegradation studies when values for environmental factors are not known, and may be more appropriate than second-order kinetics when values for environmental factors are known.

INTRODUCTION

The fate of petroleum hydrocarbons in sediment environments has been reported by numerous authors (Harrison and others, 1971; Atlas, 1981; Floodgate, 1984; Chang and others, 1985; 1986; National Research Council, 1985; Chang, 1987; Chang, Noben, and Bullert, 1987; Chang, Hult, and Noben, 1987; Chang and Bullert, 1988; Chang and Wang, 1989), but little research has been done on kinetics of crude-oil biodegradation by indigenous microbes mediated by various environmental factors. Such research is especially relevant to ground water and deep subsurface environments. The second-order model of Monod kinetics can be used to predict the biodegradation of crude oil in a ground-water environment, but this model does not include many environmental factors. Therefore, a number of mathematical models were proposed in this study to describe the kinetics of the biodegradation of crude oil as affected by a variety of environmental factors, such as concentration of crude oil (substrate), concentration of inorganic nutrients (nitrogen and phosphorus), population density of crude-oil-degrading bacteria, concentration of dissolved oxygen, and temperature. These kinetic models may prove to be a better quantitative tool than Monod kinetics for predicting changes of rates of biodegradation in ground-water conditions.

In this study, static and microcosm systems were used to conduct experiments of crude-oil biodegradation by indigenous microorganisms over a period of 6 months. Also, kinetic models were developed to predict rates of biodegradation of crude oil in ground-water environments. This paper presents the results of the experiments.

MATERIALS AND METHODS

Ground-water and sediment samples were collected from an oil-spill site near Bemidji, Minn. (fig.1). Populations of crude-oil-degrading bacteria were enumerated by the five-tube, most-probable-number technique using modified Tauson's broth medium with a substitution of crude oil as a sole source of carbon and energy (Atlas, 1981; Chang and Ehrlich, 1984; Chang and others, 1985; Chang, Hult, and Noben, 1987).

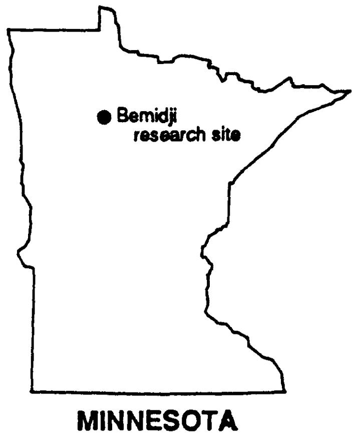

Figure 1. Location of Bemidji research site, Minnesota.

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Biodegradation experiments of crude oil were conducted using both a microcosm system that was incubated at four temperature regimes and static systems at room temperature. In the static system, quadruplicate 500-mL (milliliter) Mason[3] jars were filled with a 200 g (grams) of sediment and 50 mL of ground water. Crude oil was added to the sediment/ground water mixture to attain an oil concentration of either 200 or 400 milligrams per kilogram. The carbon dioxide (CO_2) evolution from each jar was measured by titration at 3 to 14 days intervals for 6 months. The microcosm system consists of triplicate 8-cm (centimeter) diameter, 14-cm-long glass cylinders filled with 600 g of sediment and 150 mL of ground water. Crude-oil additions and CO_2-evolution measurement were as described in the static system. The samples were incubated at 2, 7, 12 and 17 °C (degrees Celsius) for 6 months. The design of microcosm, procedures, and methodology have been reported earlier by Chang and Broadbent (1981), Chang and Alexander (1983), and Chang, Hult, and Noben, 1987.

The Monod equation (Monod, 1949) was applied to describe the rate of substrate consumption by indigenous crude oil-degrading bacteria grown in static or microcosm systems. According to Monod,

$$\frac{d[N]}{dt} = \frac{U_{max}[N][S]}{K_s + [S]} \tag{1}$$

where U_{max} is the maximum specific growth rate (per hour), [N] is the population density (number per milliliter) of the oil-degrading bacteria, [S] is the concentration of the substrate (crude oil concentration, in micrograms per liter), t is the incubation time (days) and K_s is the rate constant for the disappearance of the substrate (in micrograms per liter). When the growth rate is 1/2 U_{max}, $Ks = [S]$. Equation 1 can be modified by adding a microbial yield coefficient Y--

$$Y = \frac{d[N]}{d[S]} ,$$

where Y expresses the conversion efficiency of substrate into microbial biomass. Multiplication of equation 1 by 1/Y changes equation 1 to an expression for the loss of [S], and equation 1 may be rewritten as

$$-\frac{d[S]}{dt} = \frac{U_{max}[N][S]}{Y\,(K_s + [S])} . \tag{2}$$

Because the crude oil added to the system served as the sole source of carbon and energy and was available through mass-transfer processes, the concentration of substrate, [S], was much greater than K_s; therefore, $Ks + [S]$ approximates [S], and equation 2 can be reduced to

$$\frac{-d[S]}{dt} = \frac{U_{max}[N]}{Y} . \tag{3}$$

Four assumptions were made in this study: (1) Crude oil is solubilized before its assimilation; (2) final products help the dissolution and mineralization of crude oil; (3) biodegradation occurs by metabolism and cometabolism simultaneously; and (4) numerous populations of indigenous microorganisms are capable of utilizing crude oil and other carbon sources present in the sediment/ground water.

A variety of environmental factors were examined to determine their effect on biodegradation kinetics of crude oil: the concentration of crude oil, redox potential (or dissolved-oxygen), availability of inorganic nutrient (such as nitrogen and phosphorus), population density of crude-oil-degrading bacteria, and temperature of the environment. In order to simplify the kinetic study, the temperature parameter was treated as an independent variable and the other five parameters were treated as interdependent. Their interrelations can be expressed by the following five equations:

$$\frac{[S]}{dt} = K_1 \cdot \frac{[S]}{[N]} \cdot \frac{d[N]}{dt} + Kd \cdot [S] \tag{4}$$

$$\frac{d[Sn]}{dt} = K_2 \cdot \frac{d[S]}{dt} \tag{5}$$

$$\frac{d[Sp]}{dt} = K_3 \cdot \frac{d[S]}{dt} \tag{6}$$

$$\frac{d[N]}{dt} = K_4 \cdot \left(\frac{[N]}{[S]} \cdot \frac{[N]}{[S_n]} \cdot \frac{[N]}{[S_p]} \cdot \frac{[N]}{[DO]}\right)^{1/4} \cdot [N]^{1/4} K_5 [N] \tag{7}$$

$$\frac{d[DO]}{dt} = K_6 \cdot \frac{d[S]}{dt} , \tag{8}$$

where [S] is concentration of crude-oil in the system (in milligrams per liter); $[S_n]$ is concentration of inorganic nitrogen (in milligrams per liter); $[S_p]$ is concentration of inorganic phosphorus (in milligrams per liter); [N] is crude oil degrading population density (colony-forming units per milliliter); t is incubation time (in days); [DO] is concentration of dissolved oxygen (in milligrams per liter); K_d is crude-oil dissolution-rate constant (in milligrams per liter); K_1, K_2, K_3, K_4, K_5, and K_6 are rate constants for crude-oil degradation, nitrogen assimilation, phosphorus assimilation, change in population of oil-degrading bacteria with organic and inorganic substrates and dissolved oxygen, proliferation of oil-degrading bacteria, and dissolved-oxygen depletion, respectively. Equations 4 to 8 were solved by the fourth-order Runge-Kutta numerical method.

To calculate the degradation turnover time in relation to the maximal growth rate, the following equation was used:

$$\frac{t}{f} = \frac{(K_t + [S])}{V_{max}} + \frac{A}{V_{max}} , \tag{9}$$

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[3] The use of brand, firm, or trade names in this paper is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

where t is incubation time (in days), f is fraction of substrate degraded (in percent), Vmax is maximal biodegradation rate (in micrograms per milliliter per hour), [S] is natural unknown substrate concentration (in milligrams per liter), K_t (in micrograms per milliliter) is rate constant, and A is concentration of added crude oil (in milligrams per liter). When t/f is plotted as a function of A, the intercept on Y axis is the turnover time for mineralization at the substrate concentration. The inverse of the slope of the straight line gives the value of U_{max} (Chang and Wang, 1989).

RESULTS AND DISCUSSION

Aerobic microorganisms in the unsaturated zone degraded crude oil more readily than anaerobic microorganisms in the saturated zone, and the addition of inorganic nutrients caused a significant increase in microbial degradation of crude oil. The population of crude-oil-degrading bacteria increased 5 to 10 days after the crude oil was added and then fluctuated slightly for the duration of the experiment. The population of crude-oil-degrading bacteria correlated well with biodegradation capability (CO_2 evolution). This correlation was better with oil-degrading population (r^2=0.985) than with total microbial population density (r^2= 0.913). Microbial generation times were 30 to 46, 24 to 37, 14 to 25, and 10 to 17 hours at 2, 7, 12, and 17 °C, respectively. Thus, a 10- °C increase in temperature decreased bacteria generation time about 2.2- to 2.4-fold. Also, the lag period of bacterial cell growth and crude-oil utilization by bacteria increased at low temperature. Generally, the greatest rate of crude-oil biodegradation by bacteria occurred at 17 to 22 °C.

The results of the kinetic studies showed that U_{max} and turnover time (T_{ov}) were 0.092 to 0.291 per hour and 1.57 to 4.35 days, respectively, in samples treated with 200 mg/L (milligrams per liter) of crude oil (table 1), and 0.051 to 0.207 per hour and 1.72 to 4.49 days, respectively, in samples treated with 400 mg/L crude oil (table 2). Yield coefficients (Y) increased with increasing temperature; they were 0.12 to 0.41 and 0.14 to 0.47 for samples treated with 200 mg/L and 400 mg/L crude oil, respectively (tables 1 and 2). Both U_{max} and K_s increased with rising incubation temperature and decreased with increasing substrate concentrations. However, dissolution rates (Kd) of crude oil, as well as rate constants K_4, K_5, and K_6, increased with both increasing incubation temperature and substrate concentration. However, K_1, K_2, and K_3 rate constants decreased with incubation temperature in all cases.

The maximal biodegradation rate (V_{max}) ranged from 5.93 to 17.39 µg/mL (micrograms per milliliter) per hour, whereas the rate constant K_t varied from 0.51 to 0.99 µg/mL in samples treated with 200-mg/L crude oil; these values were lower in samples treated with 400-mg/L crude oil. Both V_{max} and K_t increased with increasing incubation temperature.

Table 1. *Kinetic rate constants for microbial activity on crude oil at a concentration of 200 milligrams per liter in a ground-water environment*

[/h = per hour; µg/L = microgram per liter; mg/L/h = milligram per liter per hour; µg/mL = microgram per milliter; µg/mL/h = microgram per milliliter per hour; °C = degrees Celsius].

Temperature (°C)	U_{max} (/h)	K_s (µg/L)	Tov (day)	Kd (mg/L /h)	K_1	K_2	K_3	K_4	K_5	K_6	Y	K_t (µg/ml)	V_{max} (µg/mL /h)
2	0.092	2.62	4.35	0.005	0.542	0.142	0.013	0.079	0.024	2.39	0.12	0.51	5.93
7	.135	3.51	2.93	.007	.493	.117	.011	.096	.031	2.52	0.19	.72	8.65
12	.204	6.32	1.96	.008	.389	.092	.008	.165	.059	2.89	0.26	.85	12.57
17	.291	10.19	1.57	.009	.381	.068	.006	.197	.064	2.95	0.41	.99	17.39

Table 2. *Kinetic rate constants for microbial activity on crude oil at a concentration of 400 milligrams per liter in a ground-water environment*

[/h = per hour; µg/L = microgram per liter; mg/L/h = milligram per liter per hour; µg/mL = microgram per milliliter; µg/mL/h = microgram per milliliter per hour; °C = degrees Celsius]

Temperature (°C)	UMax (/h)	K_s (µg/L)	Tov (day)	Kd (mg/L /h)	K1	K2	K3	K4	K5	K6	Y	K_t (µg/mL)	V_{max} (µg/mL /h)
2	0.051	1.63	4.49	0.006	0.563	0.135	0.011	0.088	0.024	2.56	0.14	0.43	5.46
7	.098	3.22	3.26	.006	.417	.117	.009	.094	.053	2.56	0.22	.66	6.98
12	.112	5.04	2.15	.009	.393	.079	.007	.215	.068	2.94	0.31	.79	10.83
17	.207	9.16	1.72	.010	.397	.068	.006	.239	.075	2.99	0.47	.97	14.45

This study indicated that the biodegradation rate conformed to fourth-order kinetics which may be as appropriate as second-order kinetics for biodegradation studies when values for environmental factors are not known, and may be more appropriate than second-order kinetics when values for environmental factors are known. This study was conducted with a high substrate concentration, so that results obtained here differ from similar biodegradation experiments performed at low substrate concentrations.

ACKNOWLEDGMENTS

This work was supported by the U.S. Geological Survey, as part of their national research project on toxic waste-ground water contamination. We are most grateful to M.F. Hult for his strong support in coordinating this research project and to Don Boyce, D. Davidson, and K. Norman for their tireless field sampling work. We are also indebted to Sharon Peterson for her skillful typing assistance.

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QUANTITATIVE STATISTICAL DESCRIPTION OF SUBSURFACE HETEROGENEITIES WITH GROUND PENETRATING RADAR AT BEMIDJI, MINNESOTA

By Gary R. Olhoeft[1]

ABSTRACT

Ground penetrating radar cross sections of the Bemidji, Minnesota, research site show details of the subsurface stratigraphy with resolution on the order of 20 centimeters to depths of 20 meters. Computer processing of the radar images has been applied to correct for the geometric distortions of the data acquisition process. Statistical analysis of the lengths of horizontally connected structures in the radar cross sections show significant geological heterogeneity across the site. In particular, the axis of one of the two petroleum plumes beneath the site (the main plume) coincides with a statistical boundary between horizontal structure lengths that are 40 meters or shorter and those that are 80 meters and longer. Parts of the site also exhibit anisotropy in the distribution of horizontal structure lengths.

INTRODUCTION

The characterization of geological heterogeneity is one of the most difficult problems in hazardous waste investigations. Inadequate knowledge of the position of boundaries between lithologies (for example, between sand and clay), stratigraphic processes (for example, deposition by eolian as opposed to fluvial processes), physical properties (for example, proportions of sand- and gravel-sized grains) and hydrologic units (for example, degree of permeability) all create uncertainties in models (Jury, 1985). Drilling does not adequately solve this characterization problem as it only yields data for points on the surface of the Earth and lines of data as a function of depth. Trenching produces much more valuable data, but it is expensive and infeasible at many sites (though routinely used in sand dune studies) (McKee, 1983). Geophysics characterizes the subsurface noninvasively and continuously in three dimensions. Of the available geophysical techniques, ground penetrating radar produces the highest resolution subsurface information. Ground penetrating radar also is the only geophysical technique found to have utility at the Bemidji, Minn., research site (Olhoeft, 1986). The Bemidji research site is described in Hult (1984); its location is shown in figure 1. This paper describes the results of use of ground penetrating radar to investigate subsurface stratigraphy at the Bemidji research site.

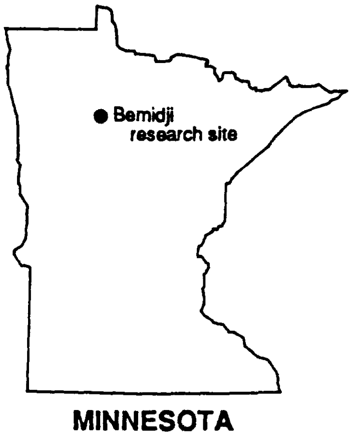

Figure 1. Location of Bemidji research site, Minnesota.

GROUND PENETRATING RADAR

Ground penetrating radar produces information about the subsurface by emitting an electromagnetic pulse and recording changes in the traveltime, amplitude, and shape of the scattered pulse. The pulse is scattered by changes in the electrical properties of the ground where the distance over which the change in properties occurs is comparable to the wavelength of the propagating electromagnetic pulse in the direction of propagation. Such scattering is principally by reflection and less commonly by diffraction. Changes in electrical properties in soils are dominantly controlled by soil bulk density and water content (Olhoeft, 1987). The relation between electrical properties, density and water content is a power law, resulting in very high sensitivity for ground penetrating radar to subtle changes in density and water content. From the surface of the Earth, the geometry of downward looking measurements gives ground penetrating radar highest sensitivity to horizontal reflectors and little or no sensitivity to vertical reflectors, which are better observed from borehole radar (Olhoeft, 1988). Further details and examples about the usage of ground penetrating radar may be found in Lucius and others (1990) and references therein.

CHARACTERIZATION OF THE BEMIDJI SITE

Several geophysical techniques have been tried over several field seasons at the Bemidji, Minn., research site. However, the only method to locate the petroleum plumes was through the use of ground penetrating radar (Olhoeft, 1986). Since that time, the emphasis on the use of geophysics has been to characterize the site.

Ground penetrating radar systems record data on digital tape and produce graphic images on gray scale imaging recorders. The gray scale images are rough cross sections of the Earth but are distorted by variations in speed of movement of the radar antenna while recording, variations in surface

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[1] U.S. Geological Survey, Denver, Colo.

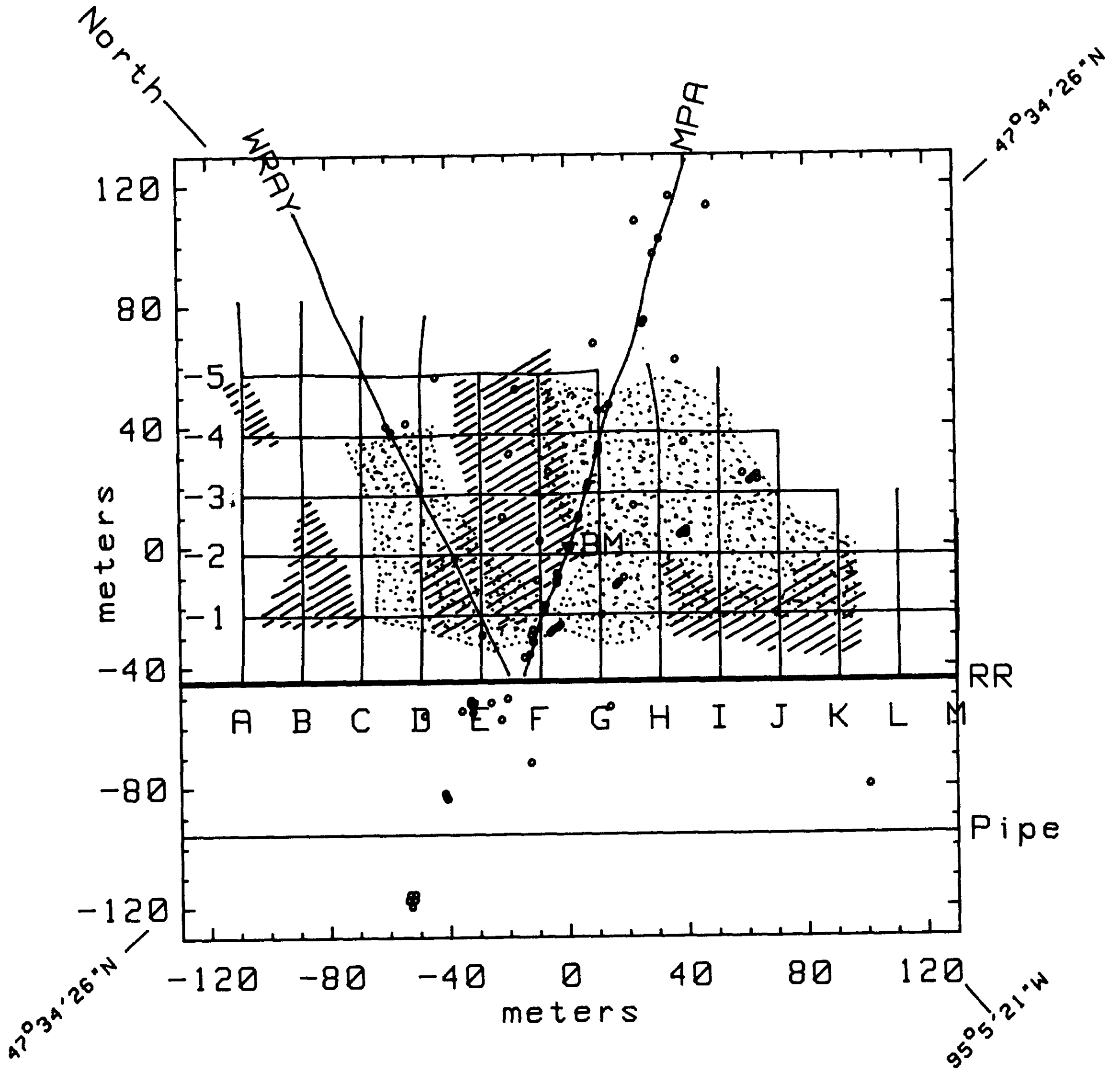

Figure 2. The statistical character of horizontal lengths from ground penetrating radar data in a direction parallel to the pipeline axis. The solid lines labeled A-M and -1 to -5 are the radar traverses. The diagonal solid line through the BM and labelled "MPA" is the main-plume-axis radar line, and the other is the "western ray." The triangle labeled "BM" is the benchmark at the local coordinate system site origin (horizontal and vertical graph axes are distance from the benchmark, in meters). Circles are wells. "RR" is the railroad tracks, and "Pipe" is the pipeline right-of-way. This plan map of the site is on the same coordinate system as figures in Bennett (1989) and others in this Proceedings. The diagonal-hachured pattern is the area of 40-meter horizontal length stratigraphy. The dotted-stippled pattern represents the area of 80-meter horizontal lengths.

topography, and variations in electromagnetic velocity in the Earth. The digital radar data are computer processed to correct for these data acquisition distortions to produce a geometrically correct cross section with resolution of 20 cm (centimeters) to depths of 20 m (meters) (see the example of the "western ray" in Bochicchio, 1988). Using such geometrically correct cross sections from the 300 megahertz center-frequency bistatic radar data, Olhoeft and others (1989) produced additional cross sections with a color code representing length of horizontally connected structure as seen by the radar. Those cross sections of horizontally connected structure were compiled and presented as histograms (compiled as structures passing through 20 X 20 X 20-m cubic volumes) of horizontal lengths in a first attempt at quantitatively describing heterogeneity at the Bemidji research site (Olhoeft and Lucius, 1990). However, such attempts were difficult to publish (because of the large color plates).

Detailed study of the horizontal length statistics thus acquired, however, suggested an alternative approach. Not all horizontal lengths were equally represented across the site. Two length scales in particular, 40- and 80-m, seemed to represent large scale differences in heterogeneity at the Bemidji site. Figures 2 and 3 show the resulting patterns of heterogeneity. In each figure, the diagonal-hachured pattern represents the area characteristic of 40-m horizontal lengths, the dotted-stippled pattern represents the 80-m horizontal lengths, and no pattern represents areas undistinguished by any particular horizontal length. The interior of each of the patterned areas may be considered to be statistically homogeneous, though each area has statistically different geological heterogeneity. Figure 2 represents the lengths observed horizontally in a direction parallel to the pipeline right-of-way, and figure 3 represents the

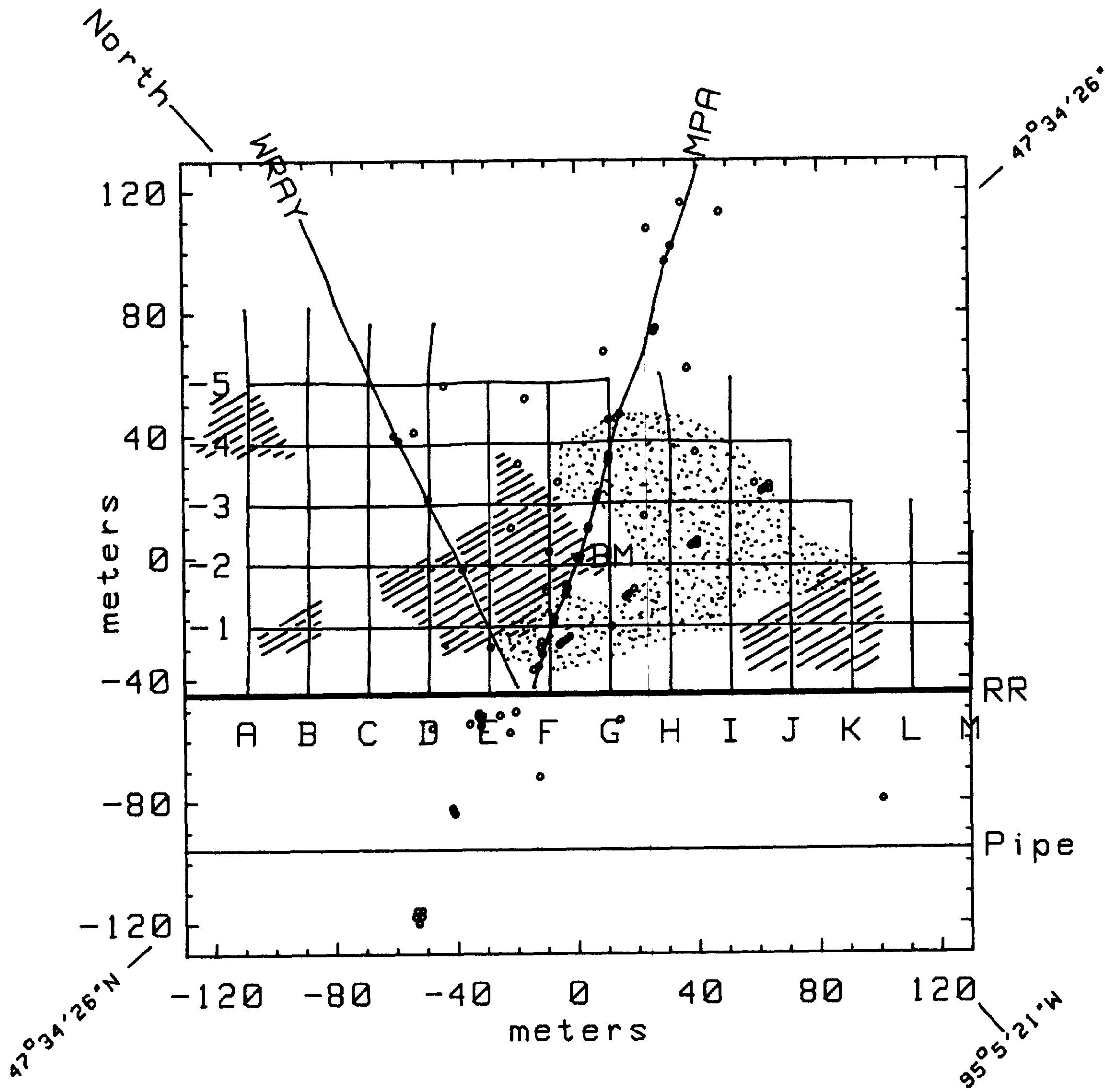

Figure 3. The statistical character of horizontal lengths from ground penetrating radar data as for figure 2, but in a direction perpendicular to the pipeline axis. The diagonal-hachured pattern is the area of 40-meter horizontal length stratigraphy. The dotted-stippled pattern represents the area of 80-meter horizontal lengths.

lengths observed horizontally in a direction perpendicular to the pipeline right-of-way. The differences in the two figures represent anisotropy. It is interesting to note that the main plume axis appears along a boundary between 40- and 80-m horizontal lengths.

CONCLUSIONS

Ground penetrating radar observes geological heterogeneity very well in soil types such as the glacial outwash at the Bemidji, Minn., research site. The principal horizons mapped by the radar appear to be till units within sandier outwash materials (Franzi, 1987). Correction of the radar data for data acquisition distortions to produce geometrically correct cross sections, produces detailed maps of site stratigraphy with 20 cm resolution to depths of 20 m. Statistical analysis of the resultant radar data delineates distinct boundaries between areas of the site characterized by 40-m and 80-m horizontal lengths. It is not yet certain why these boundaries exist, but they are probably related to the geological processes that formed and reworked the site geology (Franzi, 1987). The characterization of heterogeneity by horizontal lengths also varies with depth, but the statistics are tenuous, so that discussion of depth dependence is not warranted beyond mention that it appears. Further investigation of the potential of ground penetrating radar to characterize site heterogeneity is required to describe physical properties quantitatively (Duke, 1990) and to estimate their variability (Jury, 1985).

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SOURCES IN CRUDE OIL OF NONVOLATILE ORGANIC ACIDS DOWNGRADIENT FROM AN OIL BODY AT BEMIDJI, MINNESOTA

By K.A. Thorn[1] *and* G.R. Aiken[1]

ABSTRACT

Nonvolatile organic acids have been isolated from contaminated wells downgradient from an oil body and from an uncontaminated well upgradient from the oil body, at Bemidji, Minnesota. The nonvolatile organic acids from contaminated and uncontaminated wells were characterized by elemental analyses, molecular-weight determinations, ^{14}C dating, and ^{13}C and ^{1}H nuclear magnetic resonance spectrometry. The undegraded oil, and the saturate, aromatic, resin, and asphaltene fractions of the undegraded whole crude oil, also were analyzed by ^{13}C and ^{1}H nuclear magnetic resonance spectrometry. The nonvolatile organic acids isolated from the contaminated wells were clearly distinguishable from those isolated from the uncontaminated well. The nonvolatile organic acids downgradient from the oil body appear to be derived from the C_{18} or greater aromatic, branched chain, and cyclic components of the crude oil.

INTRODUCTION

Biodegradation of crude oil has resulted in a plume of dissolved organic carbon (DOC) downgradient from the oil body contaminating the aquifer at the Bemidji research site (fig. 1). Most of the DOC consists of nonvolatile organic acids (NVOA), which have been classified into three fractions on the basis of adsorption chromatography on XAD resins: "hydrophobic neutral" fraction of organic acids (HPO-N-A), hydrophobic acids (HPO-A), and hydrophilic acids (HPI-A). These three fractions of organic acids have been isolated from a contaminated well (530) downgradient from the oil body. Elemental analyses, molecular-weight determinations, ^{14}C ages, and ^{13}C and ^{1}H nuclear magnetic resonance (NMR) spectrometry analyses have been performed on the HPO-N-A, HPO-A, and HPI-A fractions to determine the sources in the crude oil of the NVOA fractions. The same set of analyses also were performed on the NVOA fractions comprising the naturally occurring background DOC isolated from uncontaminated well 310, upgradient from the oil body. The NMR analyses also were performed on the saturate, aromatic, resin, and asphaltene fractions of the crude oil.

EXPERIMENTAL PROCEDURE

The HPO-N-A, HPO-A, and HPI-A acids were isolated on XAD-8 and XAD-4 resins as described by Aiken and Thorn (1989). Crude oil was fractionated by adsorption chromatography on silica gel, after the asphaltenes were removed by precipitation with pentane. Number average molecular weights ($\overline{M_n}$'s) were determined from four concentration points by vapor-pressure osmometry. ^{14}C ages were obtained from A.J.T. Jull at the University of Arizona accelerator mass-spectrometry facility. NMR analyses were performed as described previously by Thorn and Aiken (1989). Distortionless enhancement by polarization transfer, GL version (DEPTGL) spectra were recorded using the pulse sequence of Sorensen and others (1983).

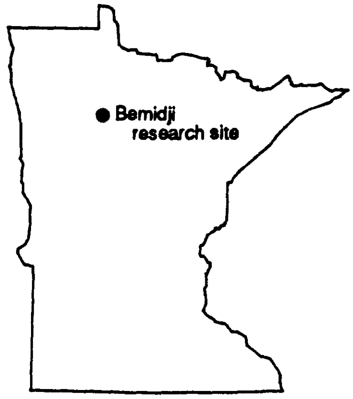

Figure 1. Location of Bemidji research site, Minnesota.

RESULTS AND DISCUSSION

Elemental analyses, ^{14}C ages, and NMR spectra indicate that the NVOA fractions from well 530 are clearly distinguishable from the NVOA fractions comprising the naturally occurring background DOC from well 310. For example, the well 530 HPO-A fraction is enriched in carbon and hydrogen but depleted in oxygen compared to the well 310 HPO-A fraction (table 1). The ^{14}C age of the well 530 HPO-A fraction is 11,661± 89 years before the present, whereas the ^{14}C age of the well 310 HPO-A fraction is post atomic bomb testing. Quantitative liquid-phase ^{13}C NMR spectra indicate that the 530 HPO-A fraction contains lesser amounts of alcohol and ether carbons (60 - 90 ppm (parts per million)) and lesser amounts of carboxylic acid carbons (170 - 190 ppm) compared to the well 310 HPO-A fraction (fig. 2). These analyses demonstrate that the NVOA's from well 530 arise primarily from the biodegradation of the crude oil, and that the contribution from the naturally occurring DOC is minor.

Number average molecular weights ($\overline{M_n}$'s) determined by vapor pressure osmometry, in combination with elemental compositional data, indicate that the well 530 HPO-N-A, HPO-A, and HPI-A fractions contain 22, 19, and 18 carbons per average molecule, respectively. Carbon distributions determined from quantitative liquid-phase ^{13}C NMR spectra

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[1] U.S. Geological Survey, Denver, Colo.

Table 1. *Elemental analyses, number average molecular weights, $\overline{M_n}$'s, and ^{14}C ages for wells 310 and 530 hydrophobic acids*

[^{14}C, carbon-14; ybp, years before present]

	C	H	O	N	S	Ash	$\overline{Mn}$ (daltons)	^{14}C age (ybp)
310 HPO-A	55.95	5.88	37.08	0.71	0.39	5.06	536	post bomb
503 HPO-A	62.18	6.75	29.09	.32	1.66	2.32	362	11,661± 89

indicate that carboxylic acid carbons comprise 6, 15, and 19 percent of the total carbons of the HPO-N-A, HPO-A, and HPI-A fractions, respectively. Aromaticities of the well 530 HPO-N-A and HPO-A fractions determined from quantitative liquid-phase ^{13}C NMR spectra indicate that these fractions are enriched in aromatic carbons relative to the undegraded whole crude oil (Thorn and Aiken, 1989). The application of ^{13}C NMR subspectral editing techniques to the well 530 HPO-N-A, HPO-A, and HPI-A fractions indicate that the fractions are depleted in methylene carbons and enriched in methyl and methine carbons relative to the whole crude oil (fig. 3). This is consistent with the preferential degradation of straight chain and simple branched hydrocarbons. Thus, the classes of compounds in the crude oil that are the sources for the NVOA's downgradient from the oil body appear to be the C_{18} or greater constituents of the aromatic, naphtheno-aromatic, acyclic isoprenoid, sterane, and triterpane fractions. The high-molecular-weight resin and asphaltene fractions of the crude oil ($\overline{M_n}$=586 and 3598 daltons, respectively) also are likely sources. Quantitative liquid-phase ^{13}C NMR spectra of the resin, asphaltene, and aromatic fractions of the crude oil are shown in figures 4, 5, and 6, respectively.

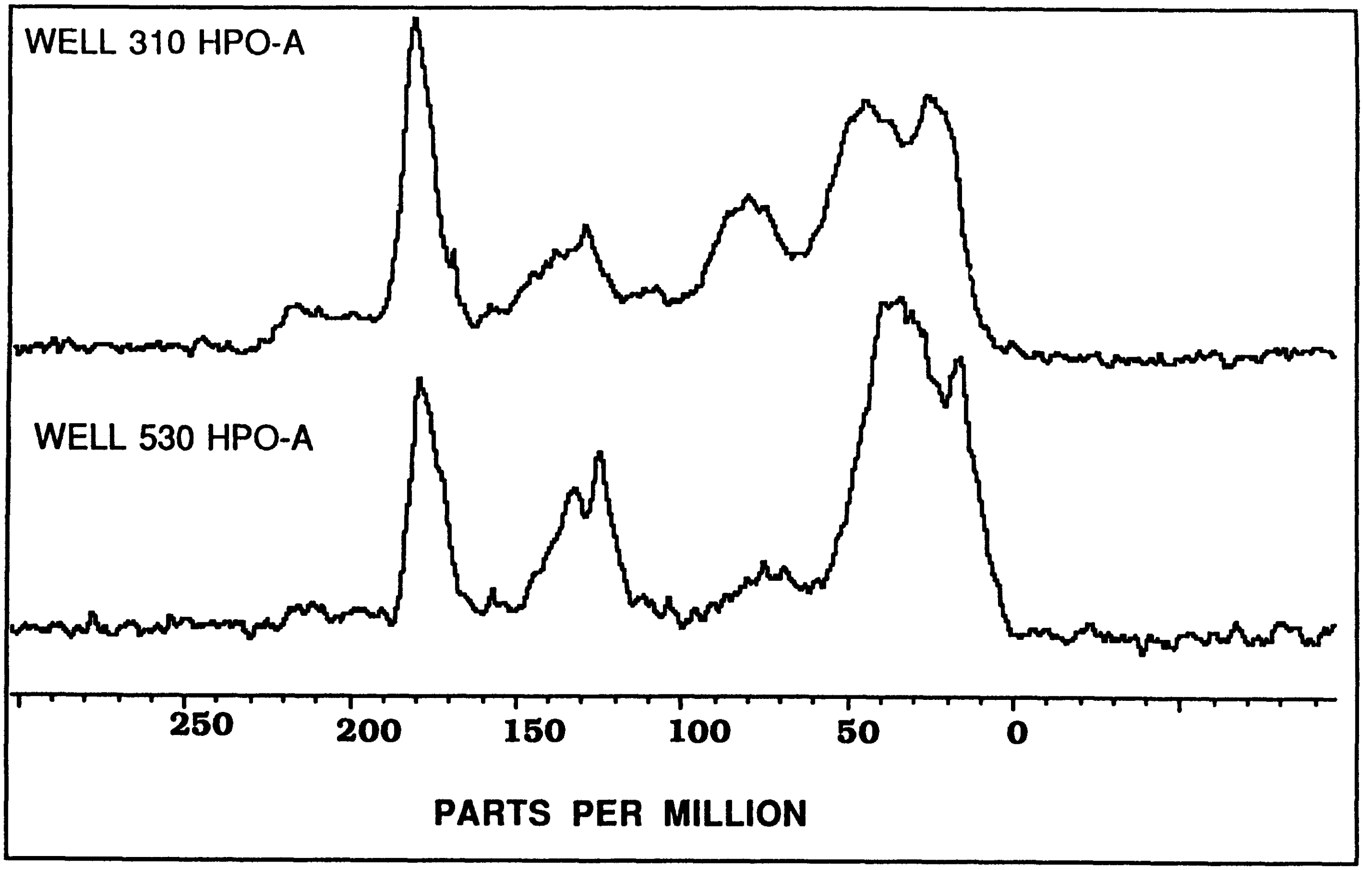

Figure 2. Quantitative liquid phase carbon-13 nuclear magnetic resonance spectra of well 310 and well 530 hydrophobic acids.

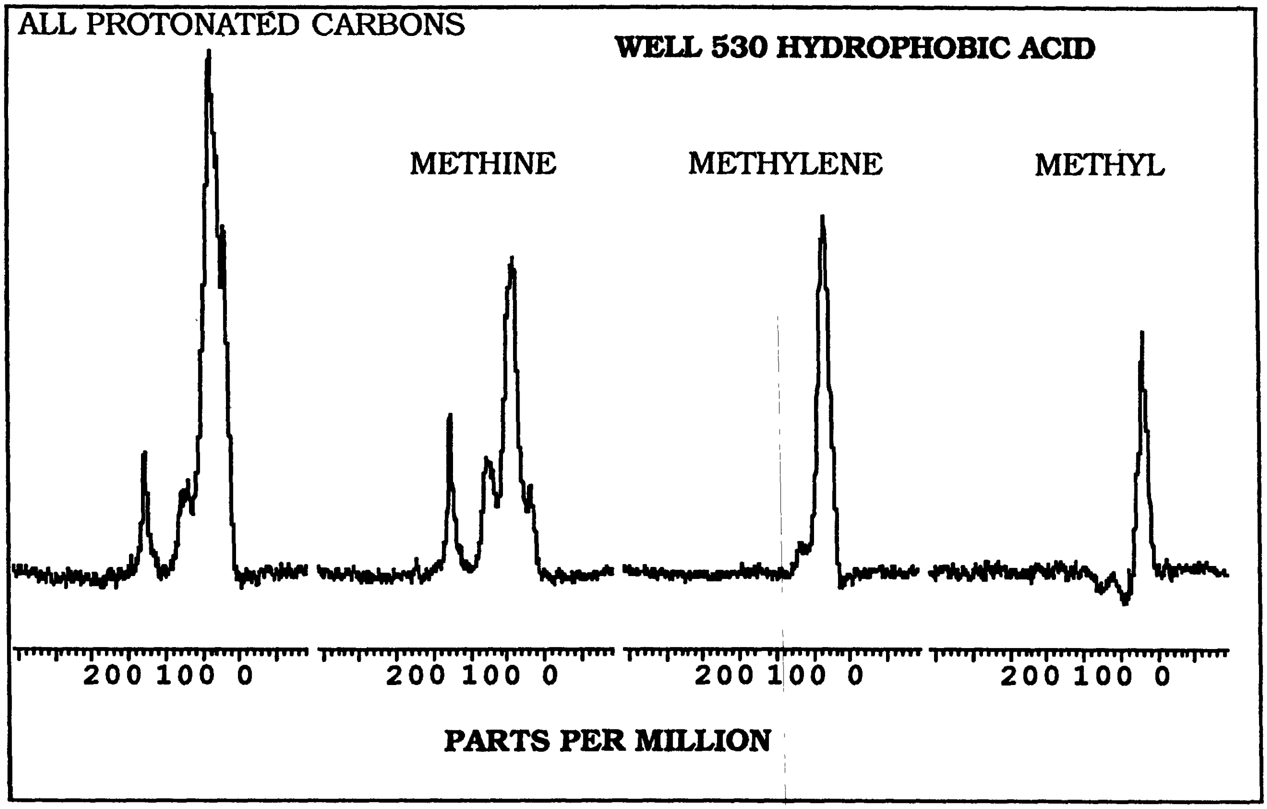

Figure 3. Distortionless enhancement by polarization transfer carbon-13 nuclear magnetic resonance spectra of well 530 hydrophobic acid.

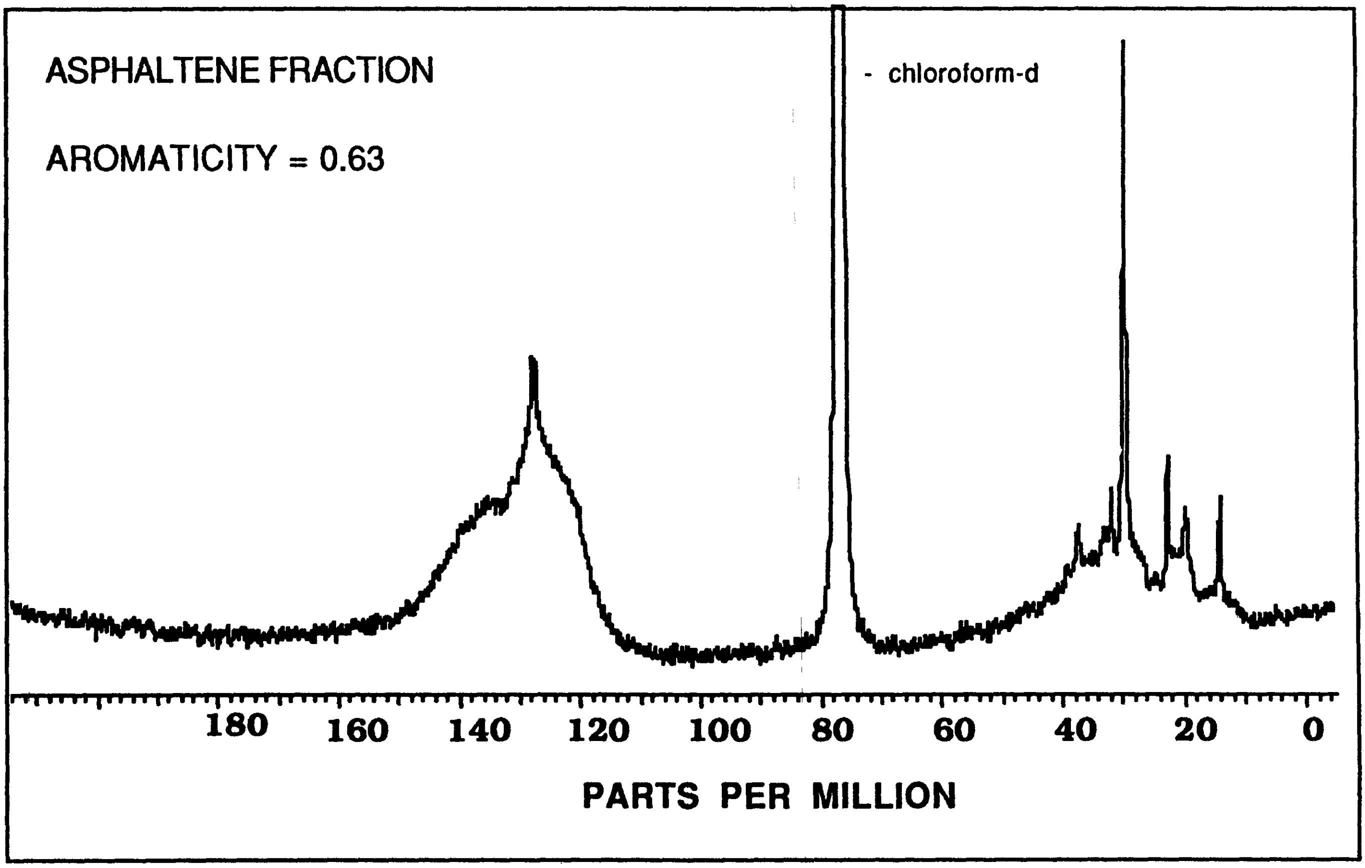

Figure 4. Quantitative liquid phase carbon-13 nuclear magnetic resonance spectrum of asphaltene fraction of crude oil.

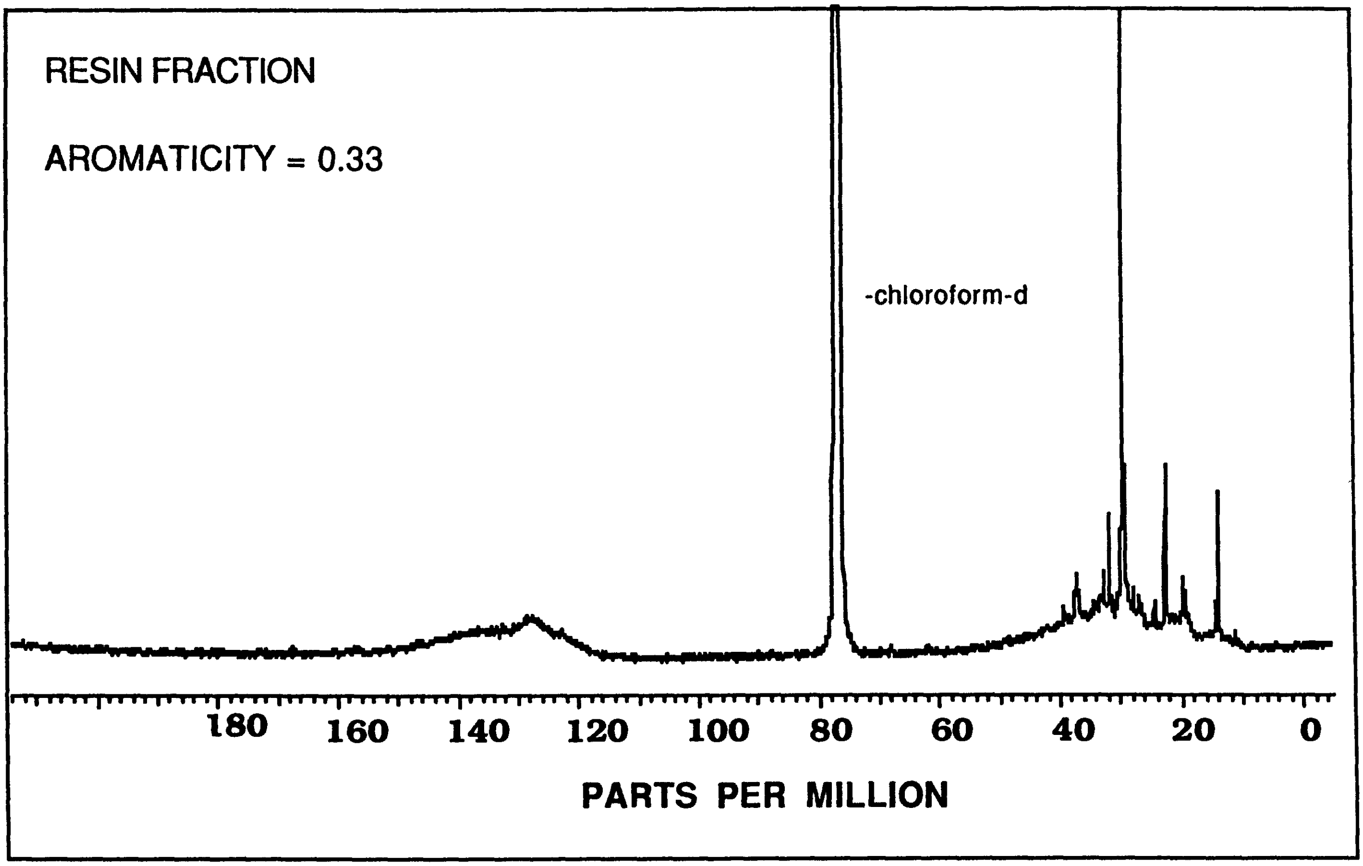

Figure 5. Quantitative liquid phase carbon-13 nuclear magnetic resonance spectrum of resin fraction of crude oil.

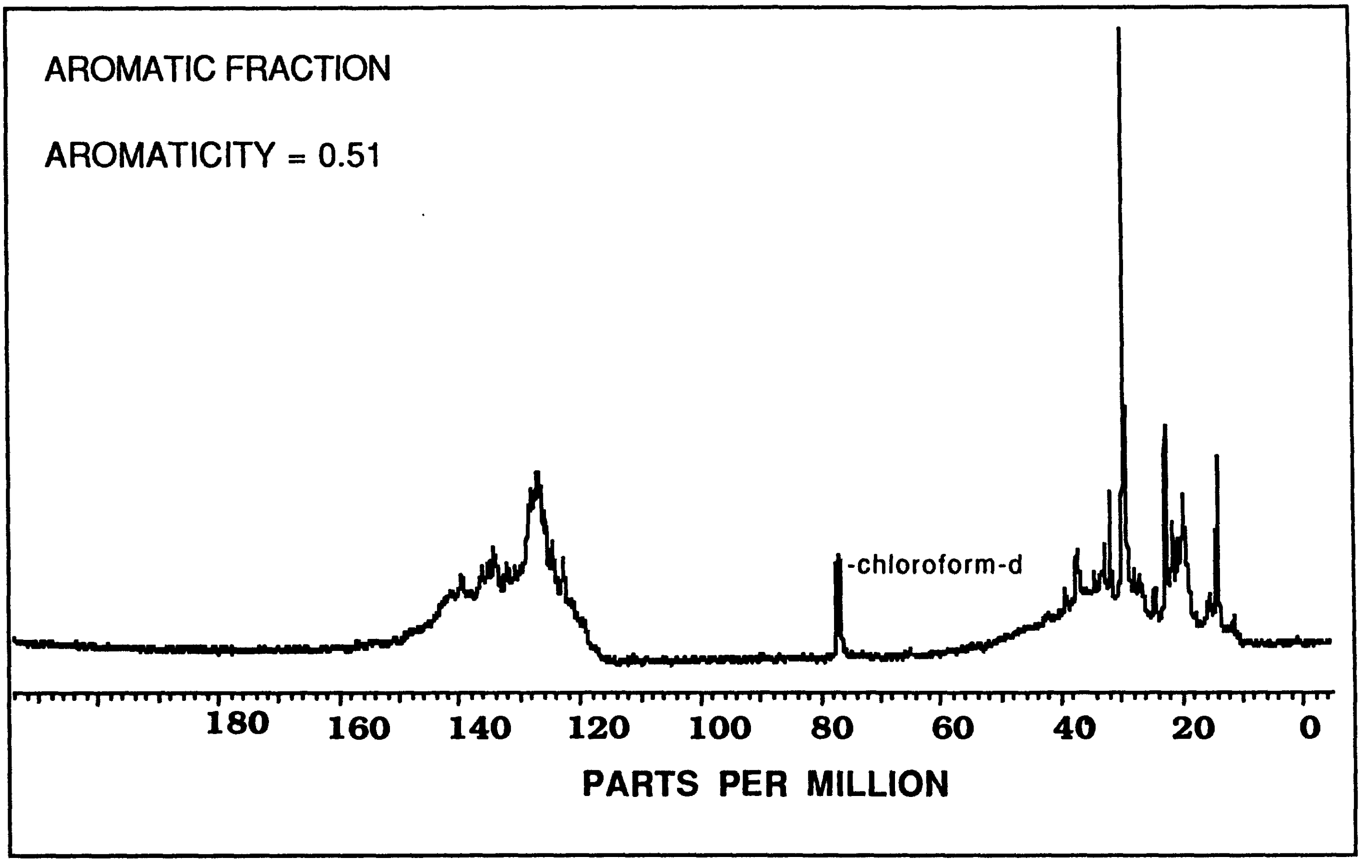

Figure 6. Quantitative liquid phase carbon-13 nuclear magnetic resonance spectrum of aromatic fraction of crude oil.

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OVERVIEW OF SAN FRANCISCO BAY ESTUARY TOXIC CONTAMINANTS STUDY

By Kathryn M. Kuivila[1] and Frederic H. Nichols[2]

ABSTRACT

The San Francisco Bay Estuary receives diverse synthetic organic and inorganic contaminants that vary widely in their environmental behavior, sources, seasonality, and toxicity. The objectives of this study are to (1) determine how organic contaminants from riverine and local sources are transported and transformed under varying hydrologic conditions (2) determine the ultimate fate of these organic contaminants and (3) develop approaches to determine whether contaminants influence ecological processes within this river-estuary system.

The primary determinants of organic contaminant distribution in the river-estuary systems are the geographic location of the source(s), the biogeochemical properties of the contaminants, and the hydrology of the system. Field studies will measure the distribution of several types of contaminants in the water column, sediments, and biota. These results, combined with laboratory studies of the biogeochemical properties of specific contaminants (for example, pesticides) and hydrodynamic modeling, can then be used to estimate distributions of organic contaminants under different conditions or in other environments.

INTRODUCTION

The estuarine system encompassing the Sacramento-San Joaquin River Delta and San Francisco Bay (fig. 1) is one of the economically and ecologically most important estuaries in the Nation (Cloern and Nichols, 1985; Nichols and others, 1986). Its drainage system includes the Central Valley of California, most of which is irrigated and intensively farmed for a diverse group of crops. Central Valley agriculture accounts for 10 percent of the total pesticide usage in the United States, comprising 20,000 tons annually and more than 500 different organic compounds (Wright and Phillips, 1988). Although pesticides are applied throughout the year, their use on different crops and application rates varies seasonally. Overall, pesticide use in the Central Valley is among the most intensive and diverse in the world. San Francisco Bay also receives municipal wastes from more than 5 million people and is an important site of petroleum refining and transport (more than 4 percent of the world total) (Risebrough and others, 1977). Thus, this estuary receives a particularly broad range of synthetic organic contaminants whose distribution is influenced by distinctly seasonal inputs of pollutants from external sources, relatively continuous inputs of pollutants from local sources, and highly variable hydrologic conditions.

The specific objectives of the San Francisco Bay Estuary Toxic Contaminants Project are to--

(1) Determine how organic contaminants from riverine and local sources are transported and transformed under varying hydrologic conditions.

(2) Determine the ultimate fate of these organic contaminants within the San Francisco Bay Estuary.

(3) Develop approaches to detect or quantify ecological responses to the presence of organic contaminants.

This paper provides background information about organic contamination in the San Francisco Bay Estuary and gives an overview of the research planned for this study.

APPROACH

The research approach is based on the presumption that the primary determinants of synthetic organic contaminant distribution in river-estuary systems are the geographic location of the source(s), the biogeochemical properties of the contaminants, and the hydrology of the system. Primary sources of contaminants to the estuary can be divided into two main categories: rivers and local sources. The Sacramento and San Joaquin Rivers, which together drain most of the Central Valley, probably account for the greatest loads of pesticides to the estuary. In effect, these two rivers are point sources of such contaminants to the estuary at Freeport and Vernalis, which are upstream from any major diversions or braiding of the river. Local sources, such as agricultural wastewater discharged from delta farmlands, are those that enter the estuary between the rivers and the ocean. Petroleum hydrocarbons from refinery effluents, urban runoff, and spills are other local sources of organic contamination.

Organic compounds can be operationally classified by two fundamental biogeochemical properties: (1) their degree of association with particles and (2) their persistence or rate of biogeochemical transformation. Laboratory studies will be used to determine the properties of relevant compounds under natural conditions. The effect of these properties on organic contaminant distribution will be examined by combining the laboratory results with field measurements.

One of the most important hydrologic characteristics of an estuary in determining contaminant loading, transport, and fate is river flow. River inflows and total freshwater discharge from the delta vary over an order of magnitude seasonally during some years and between extreme years in response to seasonal and interannual precipitation patterns (Smith, 1987). This variability, in turn, determines patterns of dilution and flushing of agricultural contaminants, transport of sediments, and circulation and mixing within the estuary. The operation of Federal and State water projects (fig. 1), which export water from the delta to the San Joaquin Valley and Southern California, modifies the natural flow regime. During much of the year, most San Joaquin River water flows to the pumping plants and the Sacramento River is the sole freshwater source to the estuary. In the winter,

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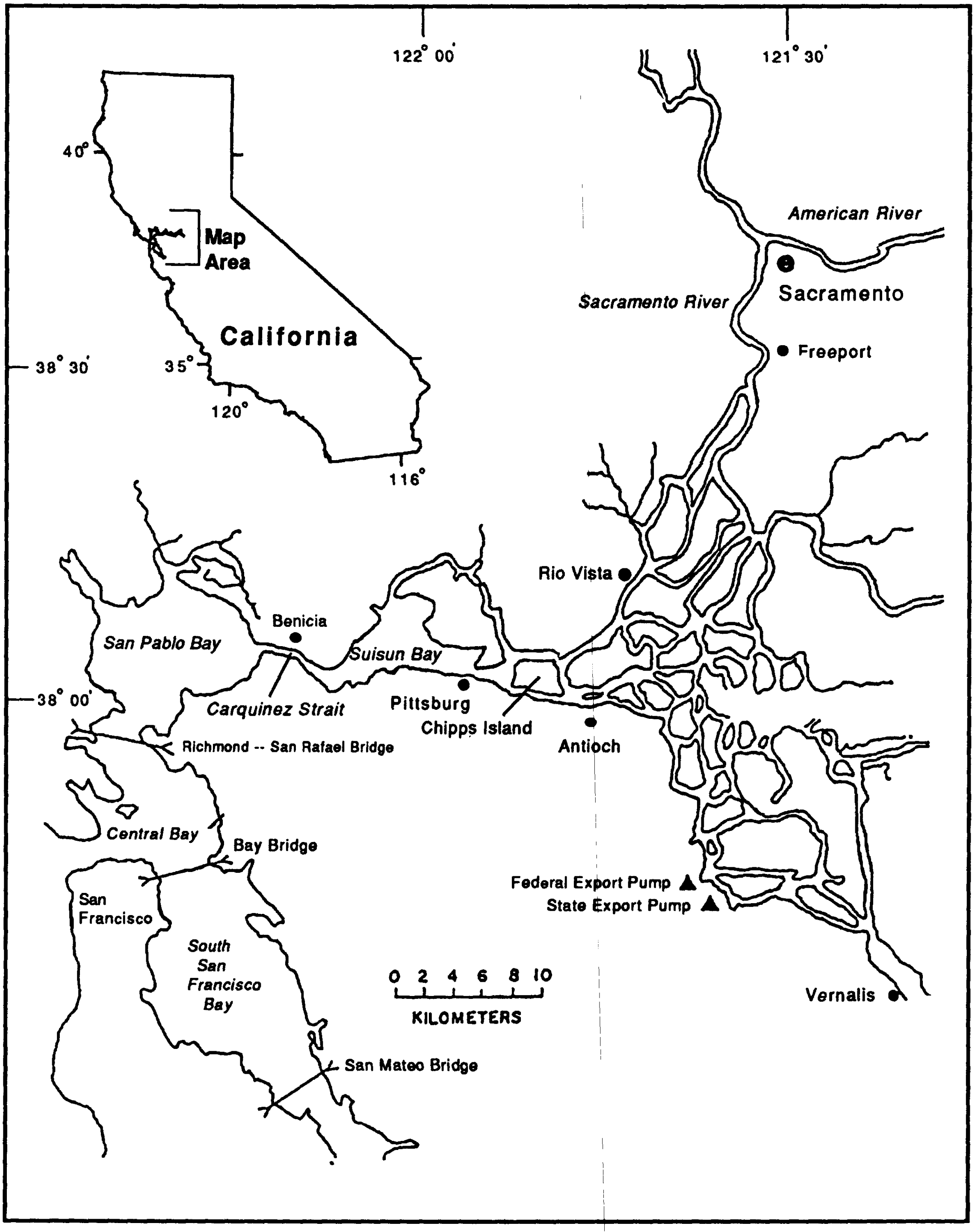
122° 00'
121° 30'
40°
Map Area
California
35°
120°
116°
38° 30'
38° 00'
American River
Sacramento
Sacramento River
Freeport
Rio Vista
Benicia
San Pablo Bay
Suisun Bay
Pittsburg
Chipps Island
Antioch
Carquinez Strait
Richmond -- San Rafael Bridge
Central Bay
Bay Bridge
San Francisco
South San Francisco Bay
Federal Export Pump
State Export Pump
Vernalis
0 2 4 6 8 10
KILOMETERS
San Mateo Bridge

Figure 1. San Francisco Bay Estuary.

typical river inflows increase significantly (greater than 35,000 cubic feet per second) (Smith, 1987), and the export pumps exert less of an effect on delta flow patterns. The combination of these seasonal and annual variations and their effect on estuarine circulation require that contaminant transport be examined over the spectrum of hydrologic conditions.

Although the major thrust of this project is to understand the transport, fate, and ecological effect of organic contaminants, previous and ongoing research on processes that affect trace elements will aid in understanding the effect on trace organic compounds (Cloern and Nichols, 1985; Luoma and Phillips, 1988; Luoma and others, 1990). Two-dimensional hydrodynamic modeling of the delta and Suisun Bay (a separate study under the Interagency Hydrodynamics Program) will be used to establish a framework to quantify transport of contaminants and predict the effect of hydrologic conditions. Ancillary measurements will provide the core of background data necessary to characterize the physical and chemical setting of the estuary during the study. The input sources of pesticides to the river-delta-bay system will be identified by seasonal and spatial studies in the river system. The distribution and transformation of pesticides will be studied in the water column and bed sediments. Petroleum hydrocarbons will be identified in sediments and biota by signatures that differentiate them from natural hydrocarbons. Effects on biota will be examined by developing an understanding of community trophic dynamics, benthic community structure, and population biology of selected species and then by comparing these processes in contaminated and uncontaminated sites (fig. 2).

Distribution and Degradation of Pesticides in the Water Column

A primary focus of the first phase of this study will be the input and distribution of the pesticides used on three major crops: rice, almonds, and alfalfa. The input of

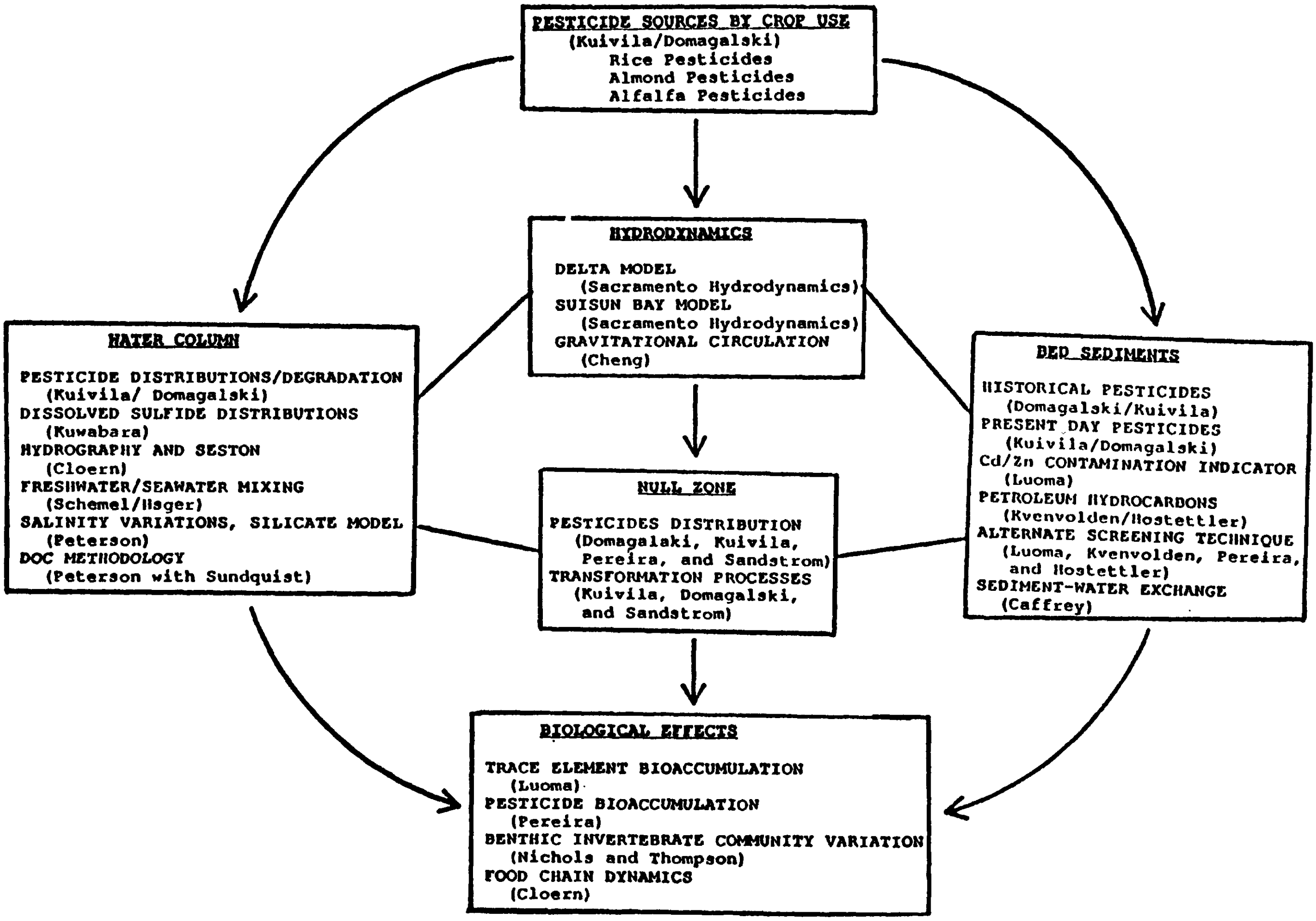
PESTICIDE SOURCES BY CROP USE
(Kuivila/Domagalski)
Rice Pesticides
Almond Pesticides
Alfalfa Pesticides
HYDRODYNAMICS
DELTA MODEL
(Sacramento Hydrodynamics)
SUISUN BAY MODEL
(Sacramento Hydrodynamics)
GRAVITATIONAL CIRCULATION
(Cheng)
WATER COLUMN
PESTICIDE DISTRIBUTIONS/DEGRADATION
(Kuivila/ Domagalski)
DISSOLVED SULFIDE DISTRIBUTIONS
(Kuwabara)
HYDROGRAPHY AND SESTON
(Cloern)
FRESHWATER/SEAWATER MIXING
(Schemel/Hager)
SALINITY VARIATIONS, SILICATE MODEL
(Peterson)
DOC METHODOLOGY
(Peterson with Sundquist)
NULL ZONE
PESTICIDES DISTRIBUTION
(Domagalski, Kuivila, Pereira, and Sandstrom)
TRANSFORMATION PROCESSES
(Kuivila, Domagalski, and Sandstrom)
BED SEDIMENTS
HISTORICAL PESTICIDES
(Domagalski/Kuivila)
PRESENT DAY PESTICIDES
(Kuivila/Domagalski)
Cd/Zn CONTAMINATION INDICATOR
(Luoma)
PETROLEUM HYDROCARBONS
(Kvenvolden/Hostettler)
ALTERNATE SCREENING TECHNIQUE
(Luoma, Kvenvolden, Pereira, and Hostettler)
SEDIMENT-WATER EXCHANGE
(Caffrey)
BIOLOGICAL EFFECTS
TRACE ELEMENT BIOACCUMULATION
(Luoma)
PESTICIDE BIOACCUMULATION
(Pereira)
BENTHIC INVERTEBRATE COMMUNITY VARIATION
(Nichols and Thompson)
FOOD CHAIN DYNAMICS
(Cloern)

Figure 2. Interactions among the various projects.

pesticides for each of these crops varies spatially and seasonally. In addition, these pesticides have varying degrees of association with particles and different rates of biogeochemical transformation. The Sacramento River receives a concentrated input of hydrophilic rice pesticides (carbofuran, methyl parathion, molinate, and thiobencarb) from agricultural drains in late May and June. A Lagrangian sampling scheme was used to measure the concentrations of these four rice pesticides and their degradation products in a single "parcel" of water (following a drogue) as it moved down the river and into the estuary in June 1990 (Domagalski and Kuivila, 1991, this Proceedings). Laboratory experiments are in progress to measure the degradation rates (both microbial and abiotic hydrolysis) of these pesticides in Sacramento River water.

The pesticides used on almond orchards are comprised of hydrophilic (ethyl parathion and diazinon) and hydrophobic (chlorpyrifos) compounds. The input of almond pesticides in February and March is primarily along the San Joaquin River. The transport and transformation of almond pesticides will be studied from the mouth of the San Joaquin River at Vernalis through the estuary using a Lagrangian sampling scheme as described above. A dye study will be used to determine traveltime from Vernalis and to determine whether most of the water flow goes directly to the export pumps or along the main river channel into Suisun Bay. The pesticides used on alfalfa fields also are comprised of hydrophilic (carbofuran, diazinon, malathion, and diuron) and hydrophobic (chlorpyrifos, endosulfan, and trifluralin) compounds. The alfalfa pesticides enter the system in April and May from locations along the San Joaquin River and from local sources within the delta. Because the input to the delta is more complex than an input from a riverine point source, this reconnaissance will consist of measuring the concentrations of alfalfa pesticides over time at various fixed sites instead of a Lagrangian study. Depending on the results from the reconnaissance studies for the three crop groups, these studies will be expanded to determine the distribution of dissolved and particulate-bound pesticides in Suisun Bay.

The rates of degradation of dissolved and particle-bound pesticides under natural conditions also will be studied in the laboratory. Microcosm experiments will be attempted to examine the rate of disappearance of added pesticides and the appearance of their degradation products in natural water and filtered, autoclaved water samples. This will result in a total degradation rate and an abiotic degradation rate with the microbial component being the difference between the two. The estimated rates of total degradation then can be integrated into the hydrodynamic models as a decay term. Changing salinity and suspended-sediment concentrations from the rivers into the estuary could have important effects on the partitioning of the pesticides between the water and particles and on the rates of degradation of the pesticides. Concentrations of dissolved and adsorbed pesticides, suspended sediment, and particulate organic carbon, and particle size will be measured along the salinity gradient. Laboratory studies will be used to evaluate the effects of salinity and suspended-sediment concentration on the partitioning between the water and the particles and on the degradation rates. With the variety of pesticides being studied, the individual effects of the geographic location of input, the biogeochemical properties, and the hydrology can be separated and identified.

Contaminants in Bed Sediments

Bed sediments integrate hydrophobic organic contaminant distributions in the water column through space and time. Short time-scale distributions (surface sediments) and long time-scale distributions (concentration profiles with depth) of pesticides and hydrocarbons in bed sediments will be examined. In the surface sediments study, the emphasis will be on present-day pesticides (endosulfan, trifluralin, and chlorpyrifos), modern petroleum hydrocarbons, and physical processes occurring on a relatively short-time scale (such as deposition, resuspension, and bioturbation). We will attempt to determine sedimentation rates (210-Pb). Microbial degradation and release of adsorbed pesticides due to reduction of iron and manganese oxide coatings on particles or degradation of organic detritus will be considered in interpreting the pesticide distributions in surface sediments. Distribution of petroleum hydrocarbons from the 1988 Shell Oil[3] spill in Martinez will be measured in the same samples and compared to the pesticide distribution.

In contrast, concentrations of organochlorine compounds of past agricultural use with long environmental half-lives (such as the dichlorodiphenyltrichloroethane (DDT) family, dieldrin, heptachlor, and chlordane) as well as trace metals, in conjunction with age dating of the sediments (210-Pb, 137-Cs, and 14-C of shells), will be determined using deeper cores in order to look at longer time-scale processes. This reservoir of buried contaminants is a potential source of long-term contaminant exposure of organisms. Data on the accumulation of these compounds in the sediments over time also will provide valuable information on the long-term ability of the estuary to filter out toxic particle-bound contaminants and on the history of contamination in the estuary.

Biological Effects

Determination of ecological response to organic contaminants will involve measurement of contaminant bioaccumulation in biota and determination of stress indicators in whole organisms, populations, and communities. These population and whole organism studies will focus on the newly dominant Asiatic clam, *Potamocorbula amurensis*. The distribution of contaminants and their degradation products will be measured in related species collected along the river-delta-estuary gradient. Bioavailability of trace organics will be studied by examining their partitioning between the water, sediments, and biota.

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[3] The use of industry or firm names in this paper is for location purposes only and does not impute responsibility for any present or potential effects on the natural resources.

The study of the effect of contaminants on community structure has two parts: (1) quantitative description of the long-term patterns in benthic community and (2) comparative assessment of growth, age structure, and reproduction at contaminated and uncontaminated sites. In the first part, population characteristics of ***Potamocorbula amurensis*** will be determined at fixed sites to define the relation with natural environmental perturbations (for example, responses to short- and long-term variations in river flow). Benthic sampling will continue in Suisun Bay to quantify population and community characteristics (reproduction, growth, secondary production, and mortality) over time. The second part involves assessing the possible effects of specific contaminants on dominant species populations. Physiological indicators of stress will be compared among populations subjected to different degrees and types of contamination by employing laboratory and field measures of respiration, growth, and reproduction as well as population indicators (age structure and dependence on external sources of recruits).

SUMMARY

The overall objective of this study is to identify and understand the processes that control the distributions, transport, fates, and ecological consequences of organic contaminants in the San Francisco Bay Estuary system. The research approach is based on the hypothesis that the primary determinants of organic contaminant distribution in the river-estuary system are the geographic location of the source(s), the biogeochemical properties of the contaminants, and the hydrology of the river-estuary system. As a major part of the study, the distribution and transformation of pesticides used on three major crops (rice, almonds, and alfalfa) will be studied in the field and in laboratory experiments. These pesticides differ in their spatial and temporal inputs and have a range of biogeochemical properties. Distributions of pesticides, petroleum hydrocarbons, and trace elements will be measured in surface and deep bed sediments to look at both short- and long-term processes. The effects of organic contaminants on biota will be examined by measuring bioaccumulation and bioavailability of the important organic compounds and by looking at variations in population biology, community structure, and physiological indicators of stress in individual animals.

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TRANSPORT AND TRANSFORMATION OF DISSOLVED RICE PESTICIDES IN THE SACRAMENTO RIVER DELTA, CALIFORNIA

By Joseph L. Domagalski[1] *and* Kathryn M. Kuivila[1]

ABSTRACT

A large quantity of pesticides and herbicides is applied to flooded ricefields in the Sacramento Valley, California, during April, May, and June. Residues of molinate, thiobencarb, carbofuran, and methyl parathion have been detected in the Sacramento River and are of concern because of their effect on aquatic life. A Lagrangian study of the transport and transformation of these compounds was made along a 45-mile reach of the Sacramento River and the tidally influenced delta. Slow degradation rates of molinate, thiobencarb, and carbofuran resulted in conservative transport during the 4-day timeframe of the study. In contrast, methyl parathion apparently was degraded in the ricefields to para-nitrophenol and only this product was detected.

INTRODUCTION

Rice is one of the most abundant crops of the Sacramento Valley of California. As much as 500,000 acres are used in the production of rice in a given year. This production is attributable partly to the abundance of high-quality irrigation water from the Sacramento River. Rice growers use a continuous-flood method of irrigation and apply a considerable amount of herbicides and pesticides from April to June. Field drain water containing dissolved residues of these compounds is discharged to the Sacramento River. Drainwater from ricefields was estimated to comprise 30 percent of the total flow in the Sacramento River during drainage of these fields (California State Water Resources Control Board, 1984).

The compounds of interest include two thiocarbamate herbicides (molinate and thiobencarb): a carbamate insecticide (carbofuran) and an organophosphate insecticide (methyl parathion). These compounds are soluble in water to concentrations of 30 to 800 milligrams per liter at 25 °C (degrees Celsius) and, therefore, are transported primarily in the dissolved phase. Residues of these compounds were detected in the Sacramento River and may have an effect on the larval stage of fish in the Sacramento River and the San Francisco Bay Estuary. California has attempted to control this discharge by prohibiting field drainage for 19 days following application of molinate.

A Lagrangian study was done on the transport and transformation of rice pesticides in a 45-mi (mile) reach of the Sacramento River downstream from the Colusa Basin Drain, one of the principal sources of ricefield drainage (fig. 1). A Lagrangian study involves following a "parcel" of water between previously chosen upstream and downstream sites. The "parcel" then can be sampled periodically and chemical reactions can be monitored within the same body of water. Typically, the inflow of the American River into the Sacramento River is significant, but during the week of the study, the inflow was low (less than 5 percent of the total). The inflow from ground water is insignificant throughout the study reach. Inflow of other sources of agricultural return water, below the Colusa Basin Drain, also are insignificant. The goals of the study were to determine the effect on the concentrations of rice pesticides by dilution and dispersion and by various degradation mechanisms which might include photolysis, hydrolysis, microbial degradation, and volatilization. A solute-transport model is being developed to quantitatively describe these processes. This paper describes the river concentrations and chemical reactions affecting the pesticides.

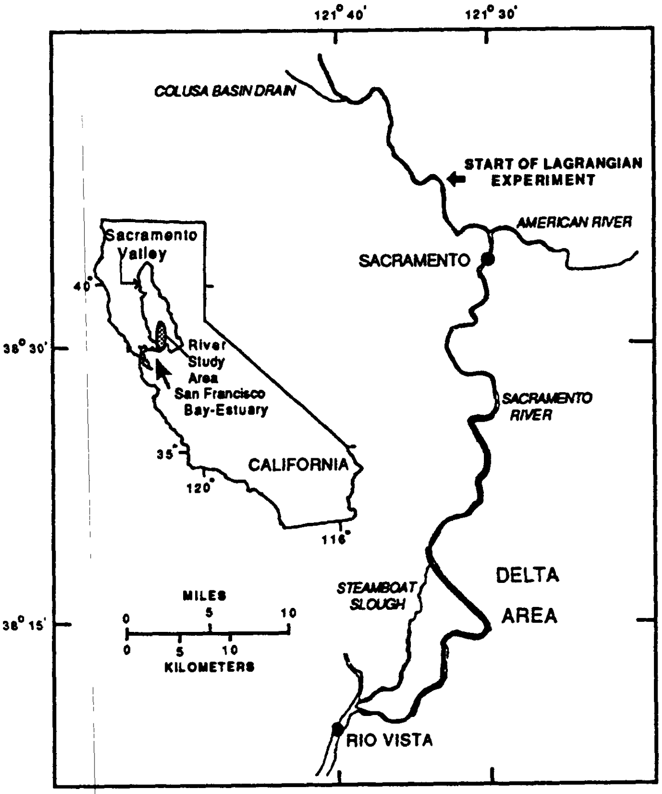

Figure 1. Study area.

The quantities of pesticides used on rice and the degradation mechanisms of the residues are listed in table 1. The pesticide-use data were collected during 1988 and are the most current data available.

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[1] U.S. Geological Survey, Sacramento, Calif.

Table 1. *Quantities of pesticides used on rice during 1988 and degradation mechanisms of pesticide residues*

Pesticide	Total pesticide application (pounds)	Degradation mechanisms
Molinate	1,467,761	Volatilization, photolysis (Soderquist and others, 1977)
Thiobencarb	421,954	Photolysis (Crosby, 1983)
Methyl parathion	71,072	Hydrolysis (Wolfe and others, 1986) or microbial degradation (Walker, 1976)
Carbofuran	58,630	Hydrolysis (Sharom and others, 1980) or microbial degradation (Chaudry and Ali, 1988)

Molinate and thiobencarb are used for control of water weeds and grasses, carbofuran is used to control rice water weevils, and methyl parathion is used to control tadpole-shrimp larvae.

METHODS

Sampling began June 3, 1990, at 1800 hours. The initial parcel of water was followed by use of a drogue, which was designed to flow with the current and be unaffected by wind. The parcel was followed through Steamboat Slough (fig. 1) instead of the main reach of the Sacramento River because that path represents the shortest traveltime to the delta. Water samples, integrated from 3 ft (feet) below water surface to a depth of 9 ft, were collected every 6 hours for a total of 96 hours. Discharge measurements and, therefore, pesticide load calculations were not made for any of the sampling stations. Because most of the study reach is tidally influenced, load calculations would require averaging discharge and concentrations over the entire tidal cycle. Load calculations are further complicated by the splitting of the waterflow between the main river channel and Steamboat Slough and other diversions. Instead, concentrations of pesticides within the "parcel" of water were plotted against time. This approach is valid because dilution of the "parcel" with surface- or ground-water inflows is not significant.

Pesticides were extracted from 2-L (liter) samples onto C_{18} solid-phase extraction cartridges and were analyzed by gas chromatography-ion trap detector (GC-ITD). Four-L samples, collected for phenolic degradation products, were extracted with dichloromethane at acid pH. Trimethyl silane derivatives of the phenols were analyzed by GC-ITD. Detection limits are as follows: molinate (100 ng/L (nanograms per liter); carbofuran (50 ng/L); methyl parathion (100 ng/L); thiobencarb (25 ng/L); carbofuran phenol (25 ng/L); and *para*-nitrophenol (50 ng/L).

RESULTS AND DISCUSSION

The results for the Lagrangian study are shown in figure 2. The points labeled as outflow near the Colusa Basin Drain are from a sample collected prior to the start of the Lagrangian study and therefore represent a separate parcel of water. Molinate, thiobencarb, and carbofuran were detected at all sampling stations. In addition, two photolysis degradation products of molinate, 2-keto molinate and 4-keto molinate, and the hydrolysis or microbial degradation product of carbofuran, carbofuran phenol, were detected. Although methyl parathion was not detected, the hydrolysis or microbial degradation product, *para*-nitrophenol, was detected. Analyses for the phenolic degradation products were not done on the Colusa Basin Drain sample.

Molinate shows a slight trend of decreasing concentrations with time (fig. 2A). The ratio of the abundance of molinate photolysis degradation products to molinate (fig. 2B) shows some scatter but no clear trend. Furthermore, the ratio in the drainwater is not significantly different than that detected in the river; therefore, these photolysis products probably were synthesized in the ricefield and photolysis is not an important reaction occurring in the river. Volatilization is the most important degradation mechanism for molinate in a ricefield (Soderquist and others, 1977), but volatilization is not an important degradation mechanism in the Sacramento River because of the much greater channel depths (20 - 30 ft) relative to the depth of a flooded ricefield (0.5 - 1 ft).

Carbofuran and thiobencarb seem to be transported conservatively (figs. 2C and 2D). Concentrations of carbofuran phenol are variable and show no clear trend (fig. 2E). A preliminary degradation experiment for carbofuran and thiobencarb showed no change in concentration in unfiltered Sacramento River water after 1 week.

Methyl parathion was not detected but its microbial or hydrolysis degradation product, *para*-nitrophenol, was detected throughout the reach of the river, suggesting that most of the methyl parathion is degraded in the ricefields. A preliminary degradation experiment for methyl parathion in unfiltered Sacramento River water suggests a half-life of 5 to 6 days. Methyl parathion is applied at about the same time as molinate and therefore is held on the ricefields for 19 days prior to drainage, allowing adequate time for significant degradation to occur.

SUMMARY

Residues of rice pesticides, either the compounds or their degradation products, were detected along a 45-mi reach of the Sacramento River. The transport seemed to be conservative. This preliminary study shows that residues of these compounds are being transported into the delta and possibly into San Francisco Bay. The transport of molinate, thiobencarb, and carbofuran is favored by slow degradation rates within the Sacramento River. In contrast, methyl parathion is rapidly degraded, probably in the ricefields, and is not detected in the river. Future work is planned on the chemical and microbial degradation of these compounds in the river-delta-bay system.

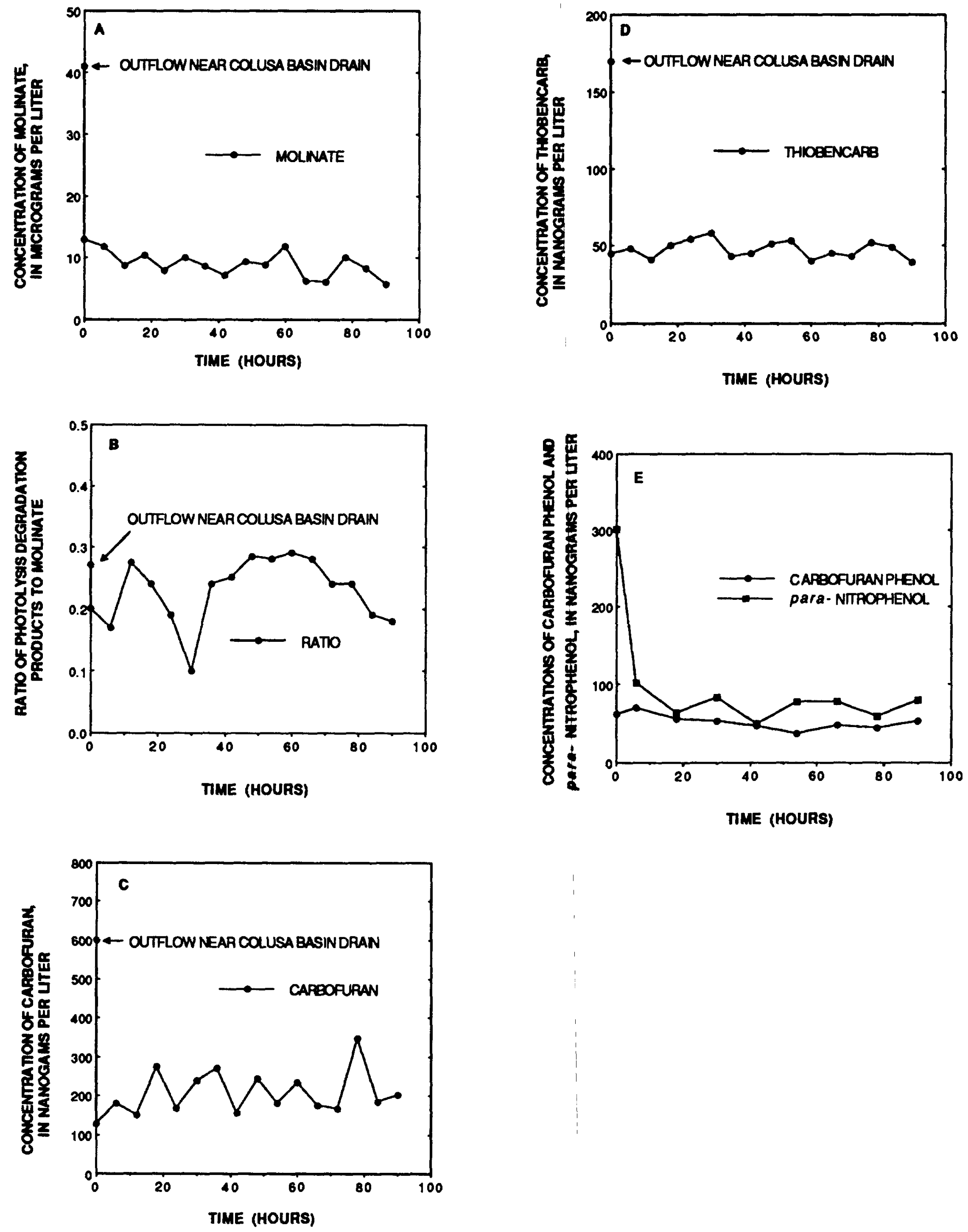

Figure 2. Results of Lagrangian study and concentrations of pesticide residues near the Colusa Basin Drain.

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ASSESSING ADVERSE EFFECTS OF CONTAMINANTS ON BENTHIC SPECIES AT THE SAN FRANCISCO BAY TOXICS SITE

By S.N. Luoma[1], J.L. Carter[1], *and* C.L. Brown[1]

ABSTRACT

Examples of adverse effects from metal exposure can be found in aquatic benthic environments at all levels of biological organization (biochemical, physiological, population, community). Conclusively demonstrating such effects in moderately contaminated environments in nature can be challenging, however. The significance of responses to metals observed at low levels of organization is difficult to demonstrate. Conclusively proving that responses at higher levels of organization are attributable solely to metal exposure is also an important challenge. Studies that do not adequately characterize pollutant exposures and do not adequately consider either the influences of environmental history or the effects of stressors other than metals can yield ambiguous results. Understanding how metals affect aquatic benthos might ultimately require studying biological responses across several levels of organization and progressively building understanding of the affected environment over time. A multidisciplinary study is using this approach in assessing effects of organic and inorganic contaminants on benthic species in San Francisco Bay.

INTRODUCTION

Biological responses to contaminants are often difficult to demonstrate in moderately contaminated environments (Bryan, 1976; Bayne and others, 1988; Ford, 1989). These difficulties result more from limited understanding than from an absence of contaminant influence. The range of spatial, temporal, and organizational scales that must be considered; the lack of baseline data from natural systems; the complexity and variety of co-occurring anthropogenic and natural disturbances; and pervasive environmental stochasticity (Kelly and Harwell, 1989; Cairns, 1990) all contribute to the challenge of detecting biological responses to contaminants.

Simple methods and simplistic approaches are perceived as necessities in defining effects of contaminants. The demand for simplicity may conflict with our crude, incomplete understanding of the complex processes by which contaminant effects are manifested in nature (Cairns, 1990; Harris and others, 1990). The purpose of this paper is to discuss interpretation of trace contaminant effects on benthic organisms in natural waters. We will emphasize the complexities that often limit interpretation of such effects. An experiment assessing contaminant effects in San Francisco Bay (fig. 1) will also be described.

Attributing a biological change in a natural system to the specific influences of metals requires (1) demonstrating which processes are sensitive to metals; (2) separating metal-induced changes in a process from background fluctuations; and (3) unambiguously relating the detected change to metal exposure rather than biotic or abiotic confounding variables. Potential confounding variables include temperature, salinity, oxygen, species interactions, and nutritional status (Livingstone, 1982). The chemical (or biogeochemical) reactions and physical processes that determine biological exposures to contaminant(s) also must be appreciated. Understanding the continuum of biochemical, physiological, population, and community responses to a contaminant exposure can facilitate proving cause and effect (Moriarity, 1988). Such understanding may also allow anticipation of the most important functional impairments in an ecosystem. The ecosystem view described above requires multidiscipline considerations that are difficult to achieve in any individual study of metal effects.

Bioaccumulation is the initial step in exposure of subcellular processes to a metal and is a necessary prerequisite to any further response. Bioaccumulation and biochemical responses are often easily detected, but their significance is difficult to determine. One cannot asssume from bioaccumulation, biochemical or physiological responses that responses at other levels of organization are occurring.

The significant effects against which aquatic communities should be protected include toxicity to individual organisms, changes in population size (or genetic composition), changes in the species that comprise a community, and changes in one or more of the local communities within an ecosystem. These are the most difficult responses to link directly with contaminants in nature (Bayne, 1985). Variance in the relevant measurements increases as biological interactions become more complex at higher organizational levels. Abiotic and biotic influences also become difficult to separate from specific metal influences, and responses may be manifested over long time scales (Depledge, 1989).

The above difficulties emphasize the inherent limitations of studying biological response to metals at any individual level of organization. In studies across several levels of organization, however, multiple lines of evidence can support conclusions (Bayne, 1985; Moriarity, 1988). Observation of a response at one level of organization also may signal that an undetectable response at the next higher level is beginning or a response is imminent. Simultaneous observation of change at a higher level of organization can verify the broader significance of the lower level response. Heretofore undefined responses to metals may lie in patterns that exist among the continuum of responses that occur across levels of organization.

EXTERNAL PROCESSES INFLUENCING METAL EFFECTS

Defining dose-response is fundamental to understanding the toxicology of a chemical. In nature, the

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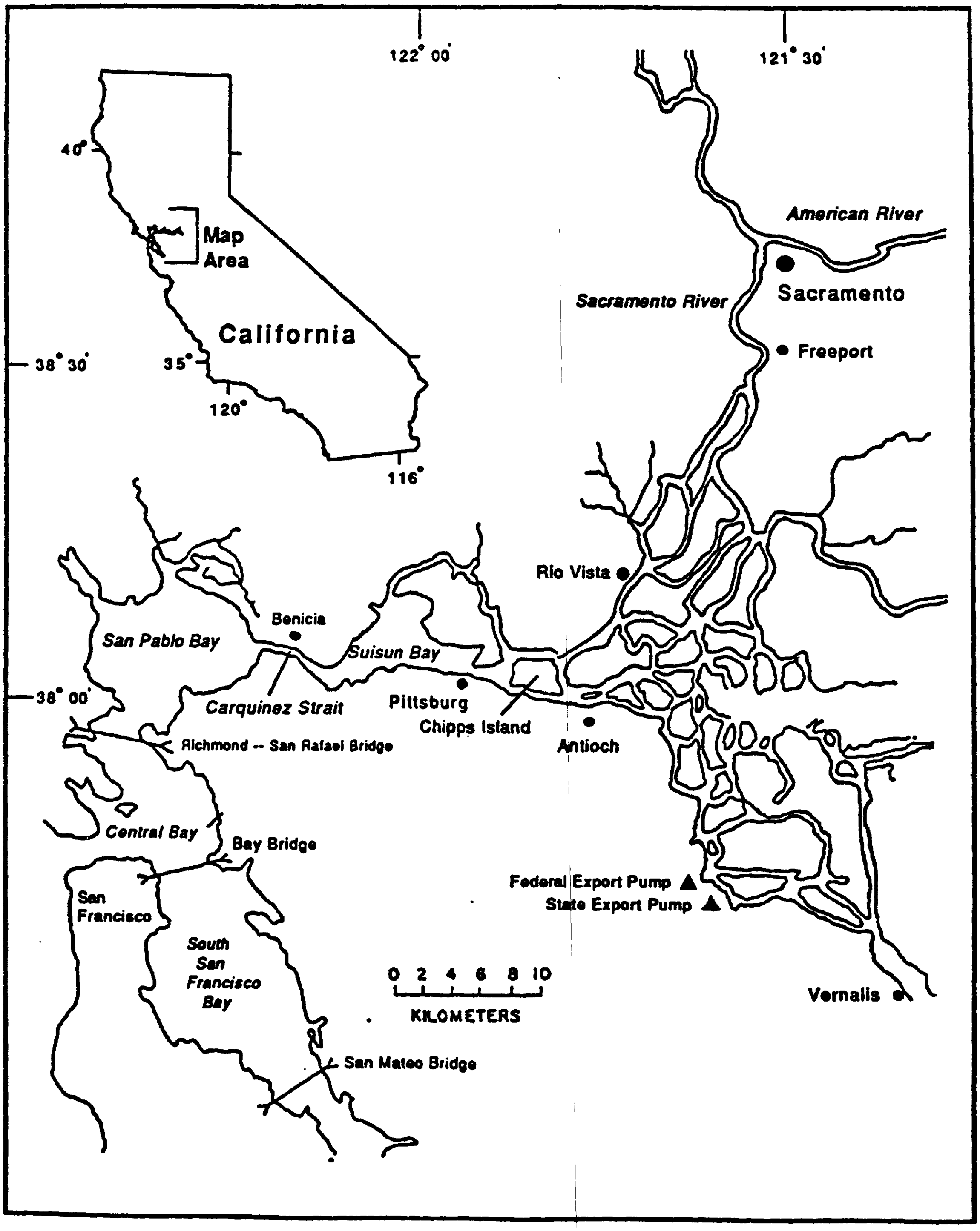
[1] U.S. Geological Survey, Menlo Park, Calif.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San Pablo Bay
Suisun Bay
38° 00'
Carquinez Strait
Pittsburg
Chipps Island
Antioch
Richmond -- San Rafael Bridge
Central Bay
Bay Bridge
San Francisco
South San Francisco Bay
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KILOMETERS
Vernalis
San Mateo Bridge

Figure 1. San Francisco Bay Estuary. (From Kuivila and Nichols, 1991.)

biological exposure to a contaminant (the dose) is not necessarily simple to define. Geochemical processes influence metal bioavailability. Anthropogenic and physicochemical influences can affect the spatial and temporal distributions of metals. Response to a contaminant also may be influenced by interactive effects of multiple contaminants, effects of multiple disturbances, or environmental history.

The most important difficulty in defining exposures in nature is that total metal concentrations in solution and sediments are not the concentrations available to biota (Sunda and Guillard, 1976; Luoma, 1983, 1989). Geochemical and biological processes determine the form of trace metals in solution or particulates. This form determines the biological availability of the metal. Predictions of metal effects are fundamentally limited by deficiencies in understanding the specific processes that govern metal bioavailability.

Concentrations of metals in sediments, water, or biological tissues are only indicators of biological exposures in nature, because bioavailability can rarely be determined directly (Luoma, 1989). A combination of all three measurements is usually most effective in estimating exposure (Moore and others, 1991). Successful studies require careful design. They should consider chemical factors such as sample contamination, analytical matrix effects, statistical design, and sample preparation. Biological factors such as choice of species, animal size, and reproductive cycle are also important considerations. The success of a field study of contaminant exposure often depends upon how explicitly hypotheses are framed.

Many field studies fail to appreciate the complexity of metal distributions in nature. Contamination gradients are not always spatially simple. Sampling that is widely scattered in time or space is rarely adequate. Available data suggest that patchy, irregular distributions are typical of contaminant concentrations in many natural systems (O'Connor and Huggett, 1988). For example, San Francisco Bay may have more than 100 contaminant "hotspots" of varying size near modern and historic sources of waste input and runoff. These hotspots create a complex spatial mosaic of contaminant exposure for resident species (Luoma and Phillips, 1988). Similar complexities are found in fluvial environments. Metal contamination is highly variable in sediments and biota in the Clark Fork River below a large copper mine. Trends are difficult to detect over reaches of less than 30 kilometers (Axtmann and Luoma, 1990). However, trends are clear through the hundreds of kilometers downstream that the metals are transported.

Temporal variability is not well studied in many systems but often must be considered. For example, episodic, seasonal and year-to-year changes in metal exposures are common in San Francisco Bay (Luoma and Phillips, 1988; Cain and Luoma, 1990). Overly simplified assumptions about spatial or temporal variability in contamination can result in chemical data inadequate to substantiate biological conclusions. Common oversimplifications include the assumption that metal concentrations are distributed in predictable gradients or that distance from the source of interest is adequate to locate "control" sites (without documentation of control exposures). One also cannot necessarily assume that exposures will not change over periods of months during a study; or that preexisting exposures were similar to those determined at the time of a study.

Contaminants are rarely found individually in a system. Multiple types of contamination can add to the difficulty of identifying the most active agents of toxicity. Little consensus exists about how the effects of multiple contaminant exposures differ from single toxicant exposures, so interpretation of the significance of multiple contaminant effects in nature is especially difficult. In the absence of adequate understanding, documentation of the presence of multiple contaminants is a minimum step in assessing biological metal effects in a field study.

Implicit in most strategies for studying effects of metals is the assumption that metals are the only factor controlling biological response. The single-minded search for the "toxic" dose may restrict consideration of abiotic or biotic processes that contribute to biological change or functional impairment. For example, biological compensation mechanisms may occur at a cost (some aspect of the biological process is weakened). If that cost is manifested when an additional stress such as a natural disturbance is imposed on the process, then functional impairment may occur in coincidence with a disturbance other than that which ultimately made the process vulnerable. Models and controlled studies both indicate that when chemicals affect filtration rate, digestion, or metabolism in starved mussels, the effects on population growth are greater than when individuals are adequately fed (Kooijman and Metz, 1984). One effect of reduced growth rates is to reduce the average size of adults in zooplankton (Meyer and others, 1987). Smaller adults may then be more vulnerable to predation and to starvation during periods of natural catastrophe. Such interactions are probably common in nature, but are difficult to detect. This level of complexity is rarely considered when the effects of metals are evaluated.

The characteristics of existing biological systems are at least partly determined by their history (Diamond, 1990). History affects the starting point from which dose-response begins when an ecosystem is contaminated by metals (Odum, 1981). History influences the kinds of species present and the tolerance of resident populations to contaminants. Thus, the sensitivity of the biological systems may differ among or within estuaries, among rivers or among coastal marine systems, depending on historical environmental characteristics, disturbances, biological interactions, or previous metal exposures (Luoma, 1977; Weis and Weis, 1989). One aim of toxicologic studies is to predict a concentration at which adverse biological effects begin in a system. Extrapolation of such studies to nature becomes more difficult if systems differ in influential historical characteristics and, thus, their inherent sensitivity. Until we begin to understand system responses to metals, we cannot approach the question of whether history influences metal responses. Nor will we understand how ecosystems and communities differ in their inherent susceptibilities to metals.

DETERMINING EFFECTS OF CONTAMINANTS IN SAN FRANCISCO BAY

Relatively few studies have convincingly demonstrated adverse effects of metals at more than one level of biological organization in a natural system. Existing methodologies seem to prove effects most successfully in acutely or severely contaminated systems (Nriagu, 1989). Many studies of specific problems in specific localities are inconclusive. A conclusion that the effects of metals are absent in a moderately contaminated system cannot be justified, however, until complexities in the overall response of biological systems to metals are considered.

In the San Francisco Bay toxics study, we are beginning a multidiscipline experiment that will assess biological responses to contaminants. Previous studies provide a base of understanding about the system (Nichols and others, 1986). The patterns of metal distribution are generally understood, and are complicated (Luoma and others, 1990). A few determinations of trace organic contaminants are available, but distributions in time and space are poorly understood. Environmental history and the predominant physical, chemical, and ecological processes have been studied for a number of years in the system. The present study will build on the existing knowledge of contaminant exposure in this system. Important goals will be to characterize selected biochemical, physiological, population, and community variables within the system and to test whether contaminants might influence the spatial or temporal distribution of these biological characteristics. We also will attempt to consider whether marginal environmental conditions might enhance biological vulnerability to contaminants; or whether processes such as selection for tolerant species or populations might reduce sensitivities of organisms.

Exposures will be determined by temporally intensive sampling of metal concentrations in sediments and bivalves at selected stations in North Bay on a monthly or bimonthly basis. The principal organism employed in the study for assessment of biochemical, physiological and population processes will be the clam *Potamocorbula amurensis* which has recently invaded the bay (Nichols and others, 1990). We will use studies of processes that influence metal bioaccumulation in this species to aid interpretation of the distributions of contaminants observed in nature. We will assess intracellular metal partitioning, while collaborating projects are studying growth, reproduction, contaminant tolerance, and population biology in this species. We will employ the complexity of the exposures to compare these processes among populations subjected to different degrees of contamination. To assess effects of several contaminants, the results of the above studies will be compared with projects studying hydrophobic organic contaminants in bivalves at a few of the stations. Exposures to pesticides also will be considered, as estimated by determinations of inputs and transport in the incoming rivers.

The choice of organism for study may allow us to test the hypothesis that the most contaminated populations will be most susceptible to natural stresses. *Potamocorbula* is in the exponential growth phase of an invasive explosion. Precedent suggests a stress-induced dieback because of natural causes is ultimately likely at the end of such an explosion. We will assess responses to such stress, should it occur, considering exposure to contaminants as an important variable.

The approach to this experiment will involve several steps--

1. Bioaccumulation processes are characterized in *Potamocorbula* so that the levels of contamination can be interpreted in terms of biological and exposure-caused effects on bioaccumulation.
2. Trace element concentrations are determined in the tissues of clams from a number of stations in San Francisco Bay in order to identify populations with different levels of contamination.
3. Bimonthly (five stations) or monthly (two stations) samples are collected so that trace element characterizations accurately reflect chronic exposures and temporal changes in metal bioavailability.
4. Procedures are developed and implemented for routinely determining metal concentrations in different subcellular biochemical fractions (cytosol compared to metals stored as inclusions).
5. Condition index, growth trends, reproductive physiology and population biology are compared over space and time among populations with different contaminant exposures (work done by several projects).
6. Changes in all the above factors are considered if a naturally induced population dieback in the species begins.
7. Controlled studies consider physiological responses to environmental factors (temperature, salinity, assimilation of food). Responses are compared among populations of *Potamocorbula* exposed to different levels of contamination, so as to more conclusively interpret that responses observed in nature.

Although our existing understanding of the effects of metals on ecosystems is limited, uncertainties can be reduced. Existing approaches commonly focus on the poorly defined regulatory goal of detecting whether metals have a biological effect. Changing focus to a more scientific goal of understanding how metals affect processes across levels of biological organization might be more profitable.

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OVERVIEW OF RESEARCH ACTIVITIES ON THE MOVEMENT AND FATE OF CHLORINATED SOLVENTS IN GROUND WATER AT PICATINNY ARSENAL, NEW JERSEY

By Thomas E. Imbrigiotta[1] *and* Mary Martin[1]

ABSTRACT

The U.S. Geological Survey is conducting an interdisciplinary research study of ground-water contamination by chlorinated solvents and other contaminants at Picatinny Arsenal, New Jersey. This paper summarizes the results of hydrogeologic and ground-water-contamination studies and describes ongoing research activities at the Building 24 site at Picatinny Arsenal.

Laboratory soil-microcosm studies were used to investigate the rates of reductive dechlorination of trichloroethylene and cis-1,2-dichloroethylene at the site. After an adaptation period of 18 weeks, most sites exhibited some degradation of cis-1,2-dichloroethylene; the maximum rate of transformation was observed at a location slightly beyond the midpoint in the flow system.

Results of laboratory column experiments showed that trichloroethylene transport in the unsaturated zone during infiltration is a nonequilibrium process. A field comparison indicated that the highest recovery of trichloroethylene from unsaturated-zone water was achieved by either collecting the sample in a gas-tight syringe or by purging and trapping the sample onsite.

A quasi-three-dimensional, finite-difference ground-water flow model of the glacial sediments and bedrock in the southern one-third of the arsenal was used to estimate hydraulic conductivity and to describe the ground-water-flow system at the contaminant site. The two-dimensional solute-transport model SUTRA was modified to simulate the transport of energy and an unlimited number of chemical species subject to user-defined chemical reactions or biological interactions.

Twenty-four wells installed in 1989 in the area of Building 24 increased the well network to 74 wells which were sampled to define in detail the contaminant plume. Results of sampling showed that neither the areal and vertical extent of the plume nor the trichloroethylene concentrations have changed significantly since October 1987.

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) improve the understanding of the chemical, physical, and biological processes that affect the movement and fate of these contaminants, particularly trichloroethylene (TCE), in the subsurface; (2) determine the relative importance of these processes; and (3) develop predictive models of contaminant transport.

In 1960, Building 24 at Picatinny Arsenal was remodeled and a new metal-plating facility and industrial wastewater-treatment plant were installed (fig. 1). From 1960-81, the wastewater-treatment system in Building 24 discharged wastewater daily into two 8-ft-(foot) deep, sand-bottomed settling lagoons behind the building (Benioff and others, 1990). The metal-plating wastewater contained trace metals, such as cadmium, chromium, copper, lead, nickel, tin, vanadium, and zinc, and other ions used in plating solutions, such as sodium, potassium, sulfate, chloride, and cyanide (Fusillo and others, 1987).

From 1973-85, an improperly installed relief system of the degreasing unit allowed pure chlorinated solvents to condense in an overflow pipe and discharge to a 4-ft-deep dry well in front of Building 24. The condensate from the overflow system contained TCE and, later (after 1983), 1,1,1-trichloroethane (Fusillo and others, 1987). The infiltration of wastewater from the lagoons and chlorinated solvents from the dry well has created a plume of contaminated ground water downgradient from Building 24.

This paper (1) describes the Building 24 research site at Picatinny Arsenal, including the hydrogeology and known extent of ground-water contamination of the aquifer system; (2) presents and discusses a conceptual model of the processes affecting the fate and transport of chlorinated solvents, particularly TCE, in the shallow aquifer at Picatinny Arsenal; and (3) summarizes the significant findings of each of the ongoing research activities at the Building 24 research site at Picatinny Arsenal.

HYDROGEOLOGY

Picatinny Arsenal is located in a glaciated valley. At the Building 24 site, 160 to 190 ft of unstratified and stratified drift overlies a weathered bedrock surface. A detailed hydrogeologic section (fig. 2) along the central axis of the contaminant plume between Building 24 and Green Pond Brook shows the presence of a 60- to 70-ft-thick unconfined aquifer. In this area, the unconfined aquifer includes several distinct but discontinuous fine-grained layers of low hydraulic conductivity. The unconfined aquifer is underlain by 25 to 70 ft of confining sediments. Near the lateral limits of the glacial sediments, the confining sediments are found in numerous discontinuous layers, and the thickness of the unconfined sediments varies greatly. The unconfined sediments range in composition from gravel and coarse sand to fine clay and peat; the confining sediments beneath and within the unconfined aquifer are composed of interbedded fine sand, silt, and clay. Based on calibration of a multilayered ground-water flow model, the estimated horizontal hydraulic conductivity of the unconfined water-table aquifer is 60 to 360 ft/d (feet per day) and the estimated vertical hydraulic conductivity of the fine-grained confining sediments is 0.01 to 0.5 ft/d (L.M. Voronin, U.S. Geological Survey, written commun., 1990).

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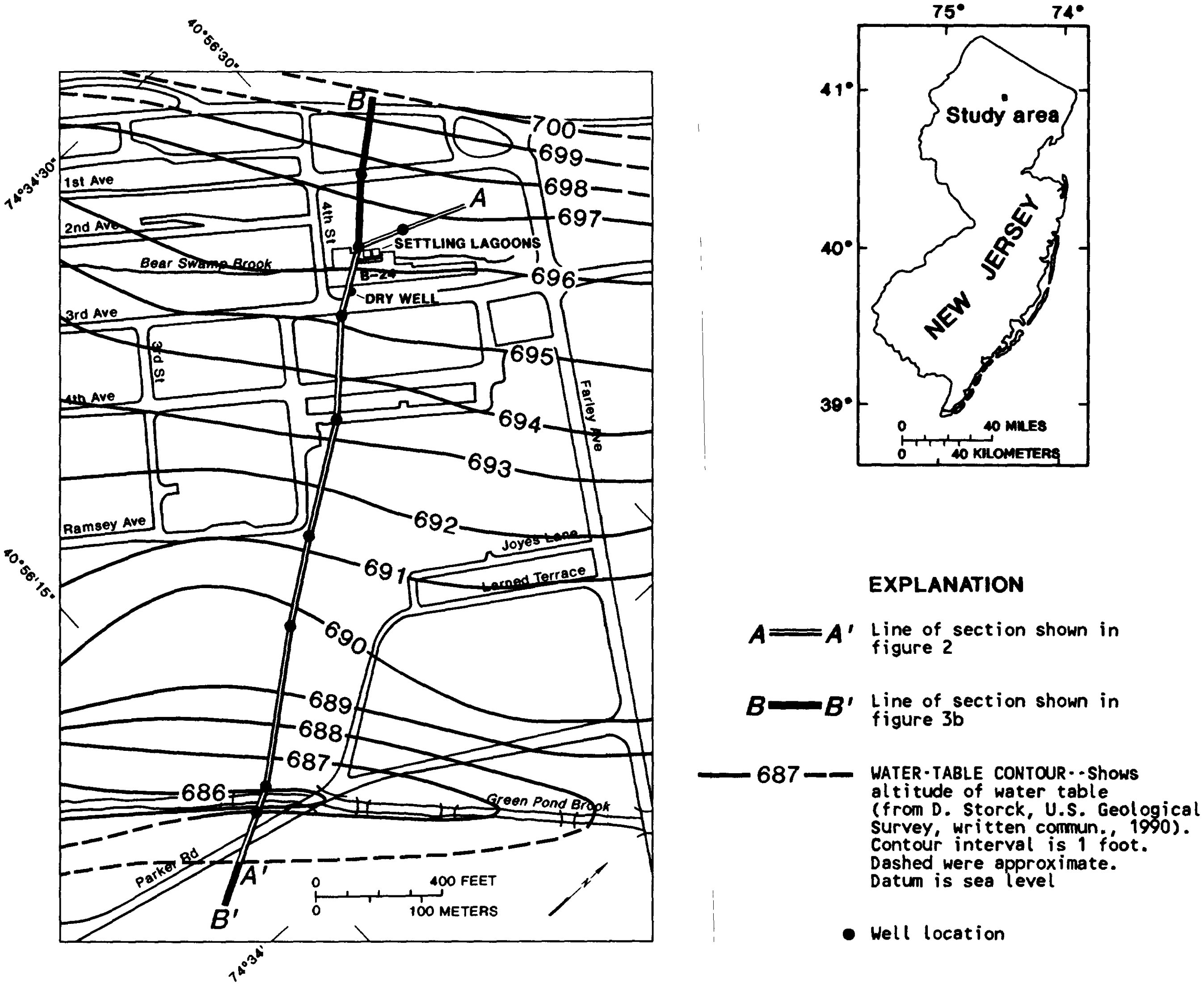

40°56'30"
74°34'30"
40°56'15"
74°34'
B
A
700
699
698
697
696
695
694
693
692
691
690
689
688
687
686
1st Ave
2nd Ave
3rd Ave
4th Ave
Ramsey Ave
4th St
3d St
Bear Swamp Brook
SETTLING LAGOONS
B-24
DRY WELL
Farley Ave
Joyes Lane
Larned Terrace
Green Pond Brook
Parker Rd
A'
B'
0 400 FEET
0 100 METERS
75°
74°
41°
40°
39°
Study area
NEW JERSEY
0 40 MILES
0 40 KILOMETERS
EXPLANATION
A——A' Line of section shown in figure 2
B——B' Line of section shown in figure 3b
—687— WATER-TABLE CONTOUR--Shows altitude of water table (from D. Storck, U.S. Geological Survey, written commun., 1990). Contour interval is 1 foot. Dashed were approximate. Datum is sea level
● Well location

Figure 1. Map showing location of Building 24 strudy area at Picatinny Arsenal, New Jersey, and altitude of the water table, April 1989.

Beneath the confining fine-grained sediments, the confined aquifer is 25 to 115 ft thick and is predominantly composed of fine to coarse sand, with some finer (silt and clay) and some coarser (gravel, pebbles, cobbles, and boulders) sediments. The underlying bedrock consists mainly of fractured dolomite of the Leithsville Formation and is separated from the overlying unconsolidated sediments by a zone of weathered bedrock of varying thickness.

The general flow pattern in the unconfined aquifer as shown by the water-table contours (fig. 1) is from the limit of the glacial sediments to Green Pond Brook, with a slight downvalley component of flow to the southwest. Within the unconsolidated sediments near Building 24, vertical flow is downward through confining sediments to the confined aquifer, then upward near Green Pond Brook, where water is discharged (fig. 2). Within the water-table aquifer, flow generally is horizontal, with some downward flow near Building 24 and upward flow near Green Pond Brook. Measured vertical head differences within the unconfined aquifer generally are less than 1 ft except near Green Pond Brook, where vertical head differences are about 3 ft. Measured vertical head gradients are 0.03 ft/ft (feet per foot) and downward between wells CAF-2 and CAF-3 and 0.22 ft/ft and upward between wells 41-8 and 41-9 (fig. 2). Measured horizontal head gradients in the water-table aquifer between Building 24 and Green Pond Brook are 0.006 ft/ft with a head difference of approximately 10 ft between these areas. Estimated ground-water flow velocities, based on calibrated flow-model hydraulic conductivities and measured head gradients, are about 5 ft/d in the plume area.

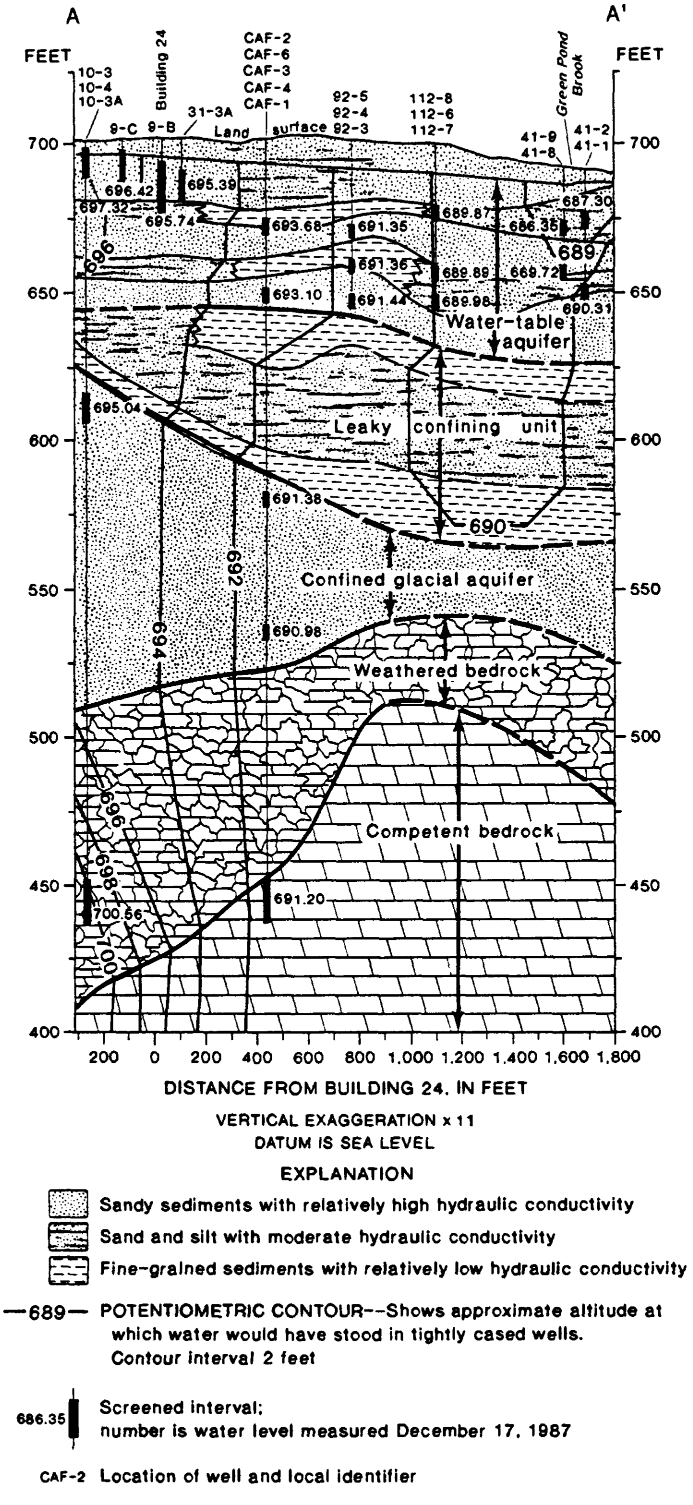

A
A'
FEET
FEET
10-3
10-4
10-3A
Building 24
9-C
9-B
31-3A
CAF-2
CAF-6
CAF-3
CAF-4
CAF-1
Land surface
92-5
92-4
92-3
112-8
112-6
112-7
Green Pond Brook
41-9
41-8
41-2
41-1
700
650
600
550
500
450
400
696.42
695.39
697.32
695.74
693.68
691.35
689.87
687.30
686.35
689
691.36
689.89
669.72
693.10
691.44
689.98
690.31
696
Water-table aquifer
695.04
Leaky confining unit
691.38
690
692
Confined glacial aquifer
694
690.98
Weathered bedrock
Competent bedrock
696
698
700.56
700
691.20
200
0
200
400
600
800
1,000
1,200
1,400
1,600
1,800
DISTANCE FROM BUILDING 24, IN FEET
VERTICAL EXAGGERATION x 11
DATUM IS SEA LEVEL
EXPLANATION
Sandy sediments with relatively high hydraulic conductivity
Sand and silt with moderate hydraulic conductivity
Fine-grained sediments with relatively low hydraulic conductivity
—689— POTENTIOMETRIC CONTOUR--Shows approximate altitude at which water would have stood in tightly cased wells. Contour interval 2 feet
686.35 Screened interval; number is water level measured December 17, 1987
CAF-2 Location of well and local identifier

Figure 2. Hydrogeologic section A-A' showing equipotential lines and approximate water-table surface, April 1989. (Location of section shown in fig. 1.)

GROUND-WATER CONTAMINATION

Chemical analysis of water from wells screened in all three aquifers suggests that most of the contamination from Building 24 has remained in the unconfined aquifer. Ground-water contamination in the unconfined aquifer has been discussed previously by Sargent and others (1986) and Fusillo and others (1987). Imbrigiotta and others (1989) and Sargent and others (1990) presented data collected in October 1987 to document the distribution of contaminants downgradient from Building 24. The most widespread contaminant in the system at that time was TCE.

Results of water-quality sampling of 51 wells in June 1989 confirmed that TCE was still the dominant contaminant in the unconfined aquifer, and that the extent of the TCE contaminant plume had changed little since October 1987. Analysis of the areal extent of the TCE plume based on the maximum concentration measured at each site (fig. 3a) shows that (1) Building 24 is the source of the TCE plume, (2) the plume extends 1,640 ft from Building 24 to Green Pond Brook, (3) the plume disperses as it moves downgradient and is approximately 1,100 ft wide where it enters Green Pond Brook, and (4) the highest concentrations of TCE are found midway between Building 24 and Green Pond Brook.

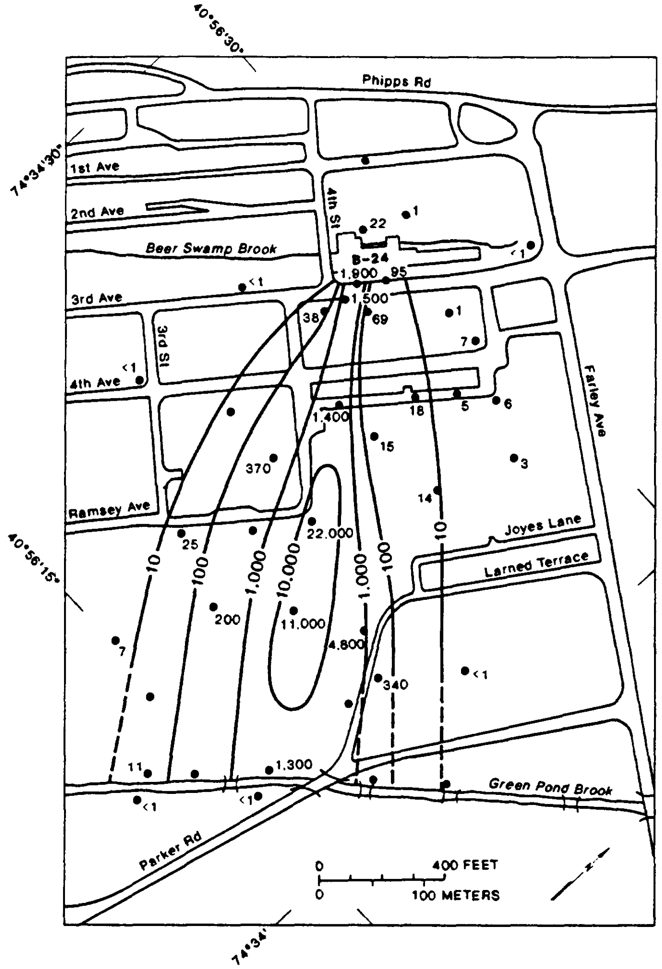
Analysis of the vertical distribution of TCE concentrations along the central axis of the plume (fig. 3b) shows that (1) the highest TCE concentrations near Building 24 are found at depths of less than 20 ft and within 35 ft downgradient from the dry well; (2) the plume follows the ground-water-head gradients as it flows downgradient, moving downward through the unconfined aquifer, then upward toward Green Pond Brook; (3) the maximum TCE concentrations in the plume are present at or near the base of the unconfined aquifer about 800 ft downgradient from Building 24; and (4) the highest TCE concentrations at Green Pond Brook are found at depths of less than 20 ft.

In addition to TCE, several other volatile organic compounds, trace metals, and other inorganic ions were found at concentrations greater than background levels in samples collected from the plume in June 1989. Additional organic and inorganic ground-water chemistry in the study area is presented in Imbrigiotta and others (1991, this Proceedings).

CONCEPTUAL MODEL

In order to guide the research efforts at the Building 24 site at Picatinny Arsenal, a conceptual model was developed to describe the physical, chemical, and biological processes that may be affecting the fate and transport of chlorinated solvents in the ground-water system (fig. 4). Solvents, like TCE, may be present in the system in many phases: dissolved in water, as a vapor in the soil gas, associated with solid surfaces or biota, and(or) as an immiscible dense nonaqueous-phase liquid (DNAPL).

Physically, the processes of advection and dispersion in the saturated zone affect the movement of both dissolved and DNAPL TCE. In addition, movement of DNAPL TCE in the saturated zone varies in response to density differences. If TCE were chemically and biologically conservative, advection and dispersion alone would control


40°56'30"
74°34'30"
40°56'15"
74°34'
Phipps Rd
1st Ave
2nd Ave
Beer Swamp Brook
3rd Ave
4th Ave
Ramsey Ave
4th St
3rd St
Farley Ave
Joyes Lane
Larned Terrace
Green Pond Brook
Parker Rd
B-24
1,900
1,500
95
22
1
<1
38
69
7
1,400
18
5
6
15
3
370
14
22,000
25
10
100
1,000
10,000
11,000
200
4,800
340
11
1,300
0
400 FEET
100 METERS

A. Areal extent of trichloroethylene contaminant plume

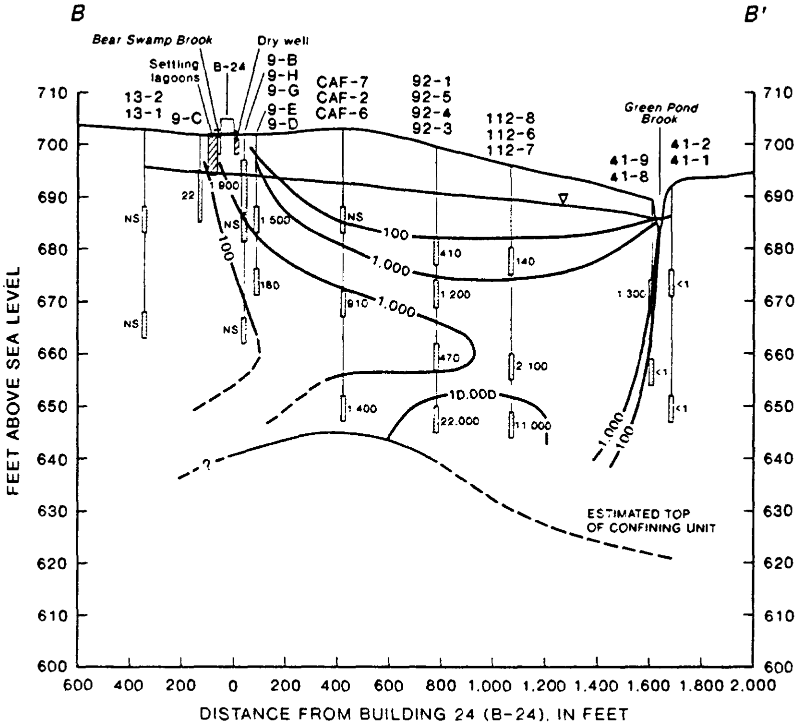
EXPLANATION

—10— LINE OF EQUAL TRICHLOROETHYLENE-CONCENTRATION--Shows trichloroethylene concentration, in micrograms per liter. Dashed where approximate.

370● Well site location and maximum trichloroethylene concentration, in micrograms per liter.

● Well site location not sampled

< Less than


B
B'
Bear Swamp Brook
Settling lagoons
B-24
Dry well
9-B
9-H
9-G
9-E
9-D
13-2
13-1
9-C
CAF-7
CAF-2
CAF-6
92-1
92-5
92-4
92-3
112-8
112-6
112-7
Green Pond Brook
41-9
41-8
41-2
41-1
710
700
690
680
670
660
650
640
630
620
610
600
FEET ABOVE SEA LEVEL
NS
22
1 900
1 500
180
100
1,000
10,000
410
140
1 200
910
470
2 100
1 300
<1
1 400
22,000
11 000
ESTIMATED TOP OF CONFINING UNIT
600 400 200 0 200 400 600 800 1,000 1,200 1,400 1,600 1,800 2,000
DISTANCE FROM BUILDING 24 (B-24), IN FEET

B. Vertical extent of trichloroethylene contaminant plume

EXPLANATION

—10— 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

Figure 3. Map showin (A) areal extent and vertical section showing (B) vertical extent of trichloroethylene contaminant plume in the Building 24 area, June 1989. (Location of section B-B' is shown in fig. 1.)

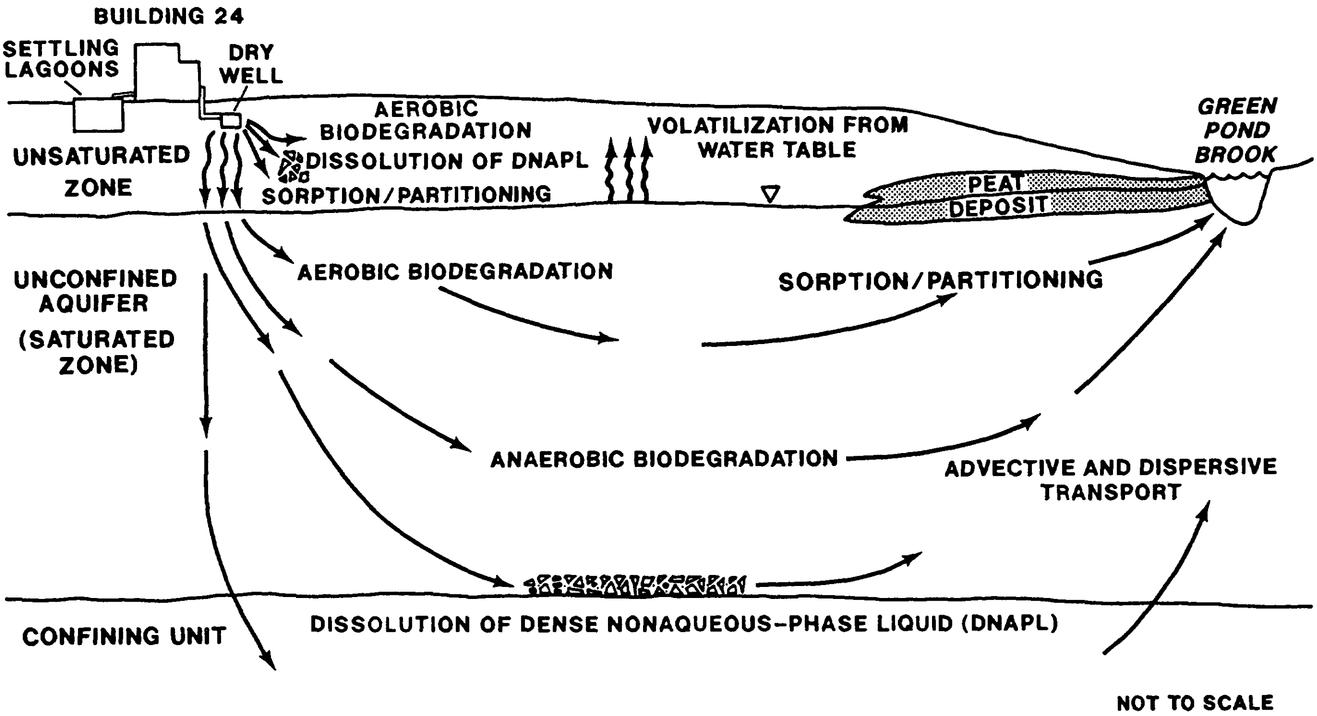

BUILDING 24
SETTLING LAGOONS
DRY WELL
AEROBIC BIODEGRADATION
DISSOLUTION OF DNAPL
SORPTION/PARTITIONING
VOLATILIZATION FROM WATER TABLE
GREEN POND BROOK
UNSATURATED ZONE
PEAT DEPOSIT
UNCONFINED AQUIFER (SATURATED ZONE)
AEROBIC BIODEGRADATION
SORPTION/PARTITIONING
ANAEROBIC BIODEGRADATION
ADVECTIVE AND DISPERSIVE TRANSPORT
CONFINING UNIT
DISSOLUTION OF DENSE NONAQUEOUS-PHASE LIQUID (DNAPL)
NOT TO SCALE

Figure 4. Schematic drawing showing conceptual model of processes affecting the fate and transport of chlorinated solvents in the ground-water system at Picatinny Arsenal.

its transport and TCE ultimately would be discharged from the aquifer to Green Pond Brook. This is not the case, however, because TCE is known to be chemically and biologically active.

Chemically, because TCE is a volatile organic compound, volatilization from ground water to the soil gas can be a potentially significant mechanism of TCE loss from the water-table aquifer (Smith and others, 1990). TCE can be both removed from and returned to the ground-water system by the process of sorption/partitioning (primarily to organic materials, such as organic coatings or peat) in both the unsaturated zone and the saturated zone (Chiou and others, 1983; Mackay and others, 1985). If TCE enters the system as a pure compound, it can be retained in the unsaturated zone or the saturated zone in a pocket of DNAPL. When water comes into contact with the DNAPL, dissolution of the pure compound can occur, and TCE can be remobilized into the system.

Biologically, TCE undergoes *in situ* anaerobic biodegradation, specifically reductive dehalogenation, by acclimated natural bacteria in many aquifer systems (Parsons and others, 1984; Kleopfer and others, 1985). Although biodegradation removes TCE from the system, it also produces breakdown products; therefore, this process also is a source of other organic compounds, such as cis-1,2-dichloroethylene (cisDCE) and vinyl choride (VC), to the system. The presence of cisDCE and VC are an indication that this process is taking place in the aquifer at Picatinny Arsenal. In addition, it has been demonstrated that TCE can be degraded cometabolically under aerobic conditions if an alternate carbon source is present in the unsaturated zone or shallow saturated zone (Wilson and Wilson, 1985; Barrio-Lage and others, 1986). Although conditions conducive to this process do not often occur naturally, unique conditions may be present in some areas of the Building 24 site that could make this process important.

CURRENT RESEARCH ACTIVITIES

Four major areas of research based on the conceptual model are being investigated at Picatinny Arsenal:

(1) Microbial transformations of chlorinated solvents in the saturated zone,
(2) Transport of chlorinated solvents in the unsaturated zone,
(3) Physical transport of chlorinated solvents through the saturated zone, and
(4) Chemical processes affecting the movement and fate of chlorinated solvents in the unsaturated and saturated zones.

A brief summary of the current research findings on each of these subjects is given in the following sections.

Microbial Transformations of Chlorinated Solvents in the Saturated Zone

The process of sequential reductive dechlorination of TCE to cisDCE to VC in the anaerobic saturated zone downgradient from Building 24 is being investigated. The primary objectives of the study are to determine biodegradation rates of TCE and cisDCE using anaerobic laboratory soil microcosms and to use these rates to represent the degradation process in a solute-transport model. The model will test whether the observed distribution of these compounds and their breakdown products in the contaminant plume can be accurately simulated. Cores were obtained from five sites contaminated with TCE and three uncontaminated sites using an aseptic drilling technique (Leach and others, 1988). Two sets of anaerobic soil microcosms were constructed--one to study the rate of degradation of TCE to cisDCE and the other to study the rate of degradation of cisDCE to VC. The experiments were designed to run for approximately 1 year. The latter experiment (cisDCE to VC) is nearing completion; the former experiment (TCE to cisDCE) is approximately half-complete. Preliminary results of the cisDCE-to-VC microcosms indicate that reductive dechlorination did occur at most sites after an adaptation period of about 18 weeks. Transformation of cisDCE at a site approximately 1,100 ft downgradient from Building 24 was nearly complete (94 percent) after 32 weeks. Only slight degradation of cisDCE occurred in soil microcosms from the uncontaminated sites during this same time interval.

A secondary objective of the study is to determine whether amendment with a series of alternate reductants (electron donors) affects the rate of biotransformation in acclimated aquifer material from the site. Again, two sets of soil microcosms have been constructed to study the effects on TCE and cisDCE separately. Electron donors being investigated are toluene, p-cresol, propionate, butyrate, and formate. Preliminary results of microcosm studies using sediments from a site known to have active biodegradation show that each electron donor seems to exert a different degree of inhibition on the biotransformation of cisDCE.

Transport of Chlorinated Solvents in the Unsaturated Zone

The transport of chlorinated solvents in the unsaturated zone is being studied with particular emphasis on the fate of volatilizing TCE vapors during infiltration. Volatilization of TCE from the water-table aquifer to the soil gas is a potential mechanism for loss of TCE from the system. Infiltrating rainfall can redissolve TCE from the vapor phase as the water comes into contact with the soil gas during percolation, however, acting as a source of TCE to the ground water. The objective of the study is to measure the volatilization rate constant of TCE from soil water to soil gas in the unsaturated zone during steady-state infiltration and to simulate this process. In the laboratory, column experiments were conducted to measure the TCE-vapor fluxes from a soil as a function of infiltration rate. Concentrations of soil-gas TCE and soil-water TCE as well as soil moisture were measured as a function of depth in the column. The principal finding so far is that the process of volatilization/redissolution is not an equilibrium process; that is, based on the concentration data obtained, it cannot be simulated with a model developed by using equilibrium assumptions. Models based on nonequilibrium assumptions are now being considered. A field experiment designed to measure the same parameters in the unsaturated zone above the TCE-contamination plume at Picatinny Arsenal currently is underway. The results will be used as input to the appropriate model to verify its applicability to "real-world" systems.

As a prelude to the infiltration field experiment, the sampling and analysis of unsaturated-zone water for TCE is required. Four sampling methods were compared to determine the method most suitable for accurate quantification of TCE concentrations. The four methods used to obtain samples of soil water are as follows: a 5-milliliter glass septum-capped vial was filled (STD), an evacuated glass septum-capped vial was filled (MBAT), a gas-tight syringe was filled (SYR), and volatile organic compounds were purged and trapped on a Tenax column in the field (P&T). Results of statistical analysis of replicate samples indicate that, on the basis of the amount of TCE recovered, the methods can be ranked in the following order: SYR = P&T>MBAT>STD.

Physical Transport of Chlorinated Solvents Through the Saturated Zone

The physical transport of dissolved chlorinated solvents through the aquifer system is being examined by using both flow and solute-transport models as investigative tools. A study to describe in detail the hydrogeologic framework of and ground-water flow in the aquifers at Picatinny Arsenal has been completed. An analysis of geophysical logs, lithologic logs, particle-size data, and test cuttings from wells installed in the southern one-third of the arsenal were used to construct detailed hydrogeologic sections, including one through the Building 24 contaminant plume. On the basis of these interpretations, six aquifer layers and five intervening low-permeability layers were defined in a quasi-three-dimensional finite-difference ground-water flow model constructed to simulate flow in the glacial and bedrock aquifers. Estimates of the horizontal hydraulic conductivities of the aquifer model layers and vertical hydraulic conductivities of the low-permeability layers were determined from model calibration. Measured water levels and simulation results indicate that the center of the TCE plume does not coincide with the area determined by the flow paths during seasons with high and low ground-water recharge rates. Generally, the center of the TCE plume is slightly farther upvalley than seasonally variable flow paths in the Building 24 area. Simulation results indicate that ground-water flow directions have a slightly greater upvalley component in the lower part of the water-table aquifer than in the upper part of the aquifer. The distribution of TCE may be, in part, the result of this vertical difference in flow paths within the water-table aquifer.

Use of solute-transport models that include solute reactions traditionally has resulted in difficulty in obtaining iterative solutions, required excessive computer and storage capacity, or oversimplified the physical or chemical processes. The objectives of a study designed to address these limitations are to develop a solute-transport model that simulates transport of an unlimited number of species, including energy, and to define their participation in chemical reactions and biological interactions. The existing SUTRA solute-transport model code (Voss, 1984) was modified to accomplish these objectives. The resulting multispecies solute-transport code also allows input of areally variable coefficients describing sorption/partitioning and production or decay. Comparison of simulations made with the modified code to previously published simulations of two and three interacting solutes and of simultaneous solute and energy transport verified that the multispecies-transport code is an accurate and useful tool for the simulation of multiple-solute movement and interaction. The multispecies-transport code will be used to simulate the fate and movement of TCE in ground water at Picatinny Arsenal, including the effects of advection, dispersion, sorption/partitioning, dissolution, microbial degradation, and volatilization.

Chemical Processes Affecting the Movement and Fate of Chlorinated Solvents in the Unsaturated and Saturated Zones

As part of a continuing effort to describe the ground-water chemistry near Building 24, 24 additional wells were installed at 10 different sites in the summer of 1989 to refine knowledge of the areal and vertical extents of the TCE contaminant plume. The complete network of 74 wells was sampled twice--in November and December 1989 and in March and April 1990. Analysis of these samples (1) improved the accuracy of the previously defined areal extent of the TCE plume, particularly at its upvalley edge near Green Pond Brook, and of the previously defined vertical extent of the TCE plume, particularly its bottom near the source and its top at the CAF-2 site (fig. 3b); (2) determined the background water chemistry upgradient from the site; (3) showed that TCE concentrations generally have not decreased significantly since October 1987; (4) confirmed by the identification of degradation products (cisDCE and VC) that reductive dechlorination of TCE is occurring in the aquifer downgradient from Building 24; and (5) revealed the presence of a site not in the center of the plume near the base of the unconfined aquifer where concentrations of TCE are greater than 10,000 micrograms per liter.

Ground water immediately downgradient from the TCE-overflow drywell in front of Building 24 is colored, difficult to filter, and contains concentrations of dissolved organic carbon (DOC) greater than 9 milligrams per liter. A study is underway to determine the origin of this water. Naturally occuring organic compounds were isolated from water samples from one well upgradient and two wells immediately downgradient from the contaminant source. The extracts, characterized by carbon-13 nuclear-magnetic-resonance analysis, were found to contain fulvic acids similar to those found in soils. The fulvic acids from the two wells with high concentrations of DOC were very similar to each other in the composition of their functional groups and in their concentrations. In contrast, these two samples differed markedly from the fulvic acids identified in the background well, which contains a much higher aliphatic-functional-group content and a lower aromatic- and carboxylic-acid-functional-group content. Water with high DOC concentrations has been hypothesized to result from the displacement of soil-pore water by DNAPL TCE that was discharged to the unsaturated zone (R.L. Wershaw, U.S. Geological Survey, oral commun., 1990).

The fairly constant TCE concentrations in the plume are evidence for a continuing source of TCE in the Building 24 area. One possible explanation is that kinetically slow desorption of TCE-contaminated aquifer sediments is taking place. A series of batch and column experiments are being planned to study the magnitude and rates of sorption/partitioning processes on soils from the source area. Another possible explanation for the persistent TCE concentrations in the Building 24 area is dissolution of pockets of DNAPL TCE. Laboratory column experiments could be used to investigate the feasibility of this hypothesis.

SUMMARY

The U.S. Geological Survey is conducting an interdisciplinary research study of ground-water contamination by chlorinated solvents and other contaminants at Picatinny Arsenal, N.J. This paper summarizes the results of hydrogeologic and ground-water-contamination studies and describes ongoing research activities at the Building 24 site at Picatinny Arsenal.

Laboratory soil-microcosm studies were used to investigate the rates of reductive dechlorination of trichloroethylene and cis-1,2-dichloroethylene at the site. After an adaptation period of 18 weeks, most sites exhibited some degradation of cis-1,2-dichloroethylene; the maximum rate of transformation was observed at a location slightly beyond the midpoint in the flow system between Building 24 and Green Pond Brook. Microcosm studies to determine the effect of various electron donors on the reductive-dechlorination process showed that each amendment tested caused a different amount of inhibition.

The process of trichloroethylene transport in the unsaturated zone during infiltration, investigated by using laboratory column experiments, was found to be a nonequilibrium process. Results of a field comparison of four methods for collecting samples of unsaturated-zone water for quantitative analysis of trichloroethylene showed that the highest recovery was achieved by either collecting the sample in a gas-tight syringe or by purging and trapping the sample in the field.

A quasi-three-dimensional, finite-difference ground-water-flow model of the glacial sediments and bedrock in the southern one-third of the arsenal was used to estimate hydraulic conductivity and to describe the ground-water flow system at the contaminant site. The two-dimensional solute-transport model SUTRA was modified to simulate the transport of energy and an unlimited number of chemical species subject to user-defined chemical reactions or biological interactions.

Twenty-four wells installed in the area of Building 24 increased the well network to 74 wells which were used to define in detail the areal and vertical extent of the trichloroethylene contaminant plume. Natural fulvic acids isolated from ground water immediately downgradient from the source had a much higher proportion of aromatic and carboxylic functional groups and a much lower proportion of aliphatic groups than fulvic acids isolated from ground water at an upgradient background site.

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CHEMICAL EVIDENCE OF PROCESSES AFFECTING THE FATE AND TRANSPORT OF CHLORINATED SOLVENTS IN GROUND WATER AT PICATINNY ARSENAL, NEW JERSEY

By Thomas E. Imbrigiotta[1], Theodore A. Ehlke[1], *and* Mary Martin[1]

ABSTRACT

Results of chemical analyses of ground water, soil gas, and aquifer sediments from a contaminant plume near Building 24 at Picatinny Arsenal, New Jersey, suggest that the fate and transport of chlorinated solvents, particularly trichloroethylene, are controlled by physical, chemical, and biological processes at the site. Nonaqueous-phase flow of trichloroethylene is suggested by both high concentrations of this contaminant near the base of the aquifer and preliminary results of solute-transport modeling. Relatively constant trichloroethylene concentrations near the source from 1987 to 1990 indicate the occurrence of slow desorption of trichloroethylene from contaminated aquifer sediments and(or) dissolution of nonaqueous-phase trichloroethylene in the aquifer. Detection of cis-1,2-dichloroethylene and vinyl chloride in 75 percent of the wells in the plume is indicative of biologically mediated reductive dehalogenation of trichloroethylene. Evidence of methanogenesis was found in 85 percent of the wells in which anaerobic reductive dehalogenation took place.

INTRODUCTION

Ground water at Picatinny Arsenal, N.J., has been contaminated during the past 30 years as a result of activities associated with metal-plating operations in Building 24. From 1960 to 1981, wastewater from the wastewater-treatment system in Building 24 was discharged into two 8-ft-(foot) deep, sand-bottomed settling lagoons behind the building (Benioff and others, 1990) (fig. 1). The metal-plating wastewater contained trace metals, such as cadmium, chromium, copper, lead, nickel, tin, vanadium, and zinc; chlorinated solvents, such as trichloroethylene (TCE); and other chemicals used in plating solutions, such as sodium, potassium, sulfate, chloride, and cyanide (Fusillo and others, 1987). From 1973 to 1985, an improperly installed degreasing-unit relief system allowed chlorinated solvents to condense in an overflow pipe and discharge to a 4-ft-deep dry well in front of Building 24. The condensate from the overflow system contained TCE through 1983 and 1,1,1-trichloroethane after 1983 (Fusillo and others, 1987). The infiltration of wastewater from the lagoons and chlorinated solvents from the dry well created a plume of contaminated ground water downgradient from Building 24 that contains both organic and inorganic chemicals. The characterization of the plume has been reported in detail by Imbrigiotta and others (1989) and Sargent and others (1990).

Since 1986, the U.S. Geological Survey has been conducting an interdisciplinary research study of ground-water contamination by chlorinated solvents at Picatinny Arsenal. The objectives of the study are to (1) identify and quantify the physical, chemical, and biological processes that affect the movement and fate of chlorinated solvents, particularly TCE, in the subsurface; (2) determine the relative importance of these processes at the site; and (3) develop predictive models of chlorinated solvent transport that may have transfer value to other solvent-contaminated sites. This paper presents chemical evidence of physical, chemical, and biological processes that affect the fate and transport of chlorinated solvents in the aquifer system at Picatinny Arsenal. This evidence is based on results of chemical analyses of ground-water and aquifer-sediment samples collected from a network of 74 observation wells and soil-gas samples collected from 16 soil-vapor probes at the Picatinny Arsenal study area during 1981-89.

METHODS

Ground-water samples were collected from a network of 74 observation wells installed in stages during 1981-89. One to four wells are located at each site shown in figure 1. At sites with more than one well, each well is screened at a different depth ranging from 16 ft to 60 ft in the unconfined aquifer.

Ground water was sampled synoptically in October-November 1987, June 1989, November-December 1989, and March-April 1990. All samples were collected according to methods described in Gibs and Imbrigiotta (1990). All samples were analyzed for field properties and constituents (temperature, specific conductance, pH, alkalinity, and dissolved oxygen), major cations and anions, nutrients, cyanide, silica, dissolved organic carbon, trace elements, dissolved methane, and purgeable organic compounds. All analyses were performed according to U.S. Geological Survey and U.S. Environmental Protection Agency protocols (Longbottom and Lichtenberg, 1982; Fishman and Friedman, 1985; Wershaw and others, 1987; Kammer and Gibs, 1989).

The purgeable-organic-compound content of the soil gas above the plume was measured by collecting samples from soil-vapor probes installed at six sites along the central axis of the plume (fig. 1). At each site, soil-vapor probes were installed at two or three different depths in the unsaturated zone. Soil gas was sampled and analyzed in February, July, October, and December 1988 by using the procedures described in Smith and others (1990).

Aquifer sediments were sampled at all sites by using either a split-spoon corer or a saturated-sand piston corer in conjunction with hollow-stem augers. Sediment subsamples were analyzed for organic carbon by using standard methods (Wershaw and others, 1987) and were used in sediment microcosms in laboratory biotransformation experiments.

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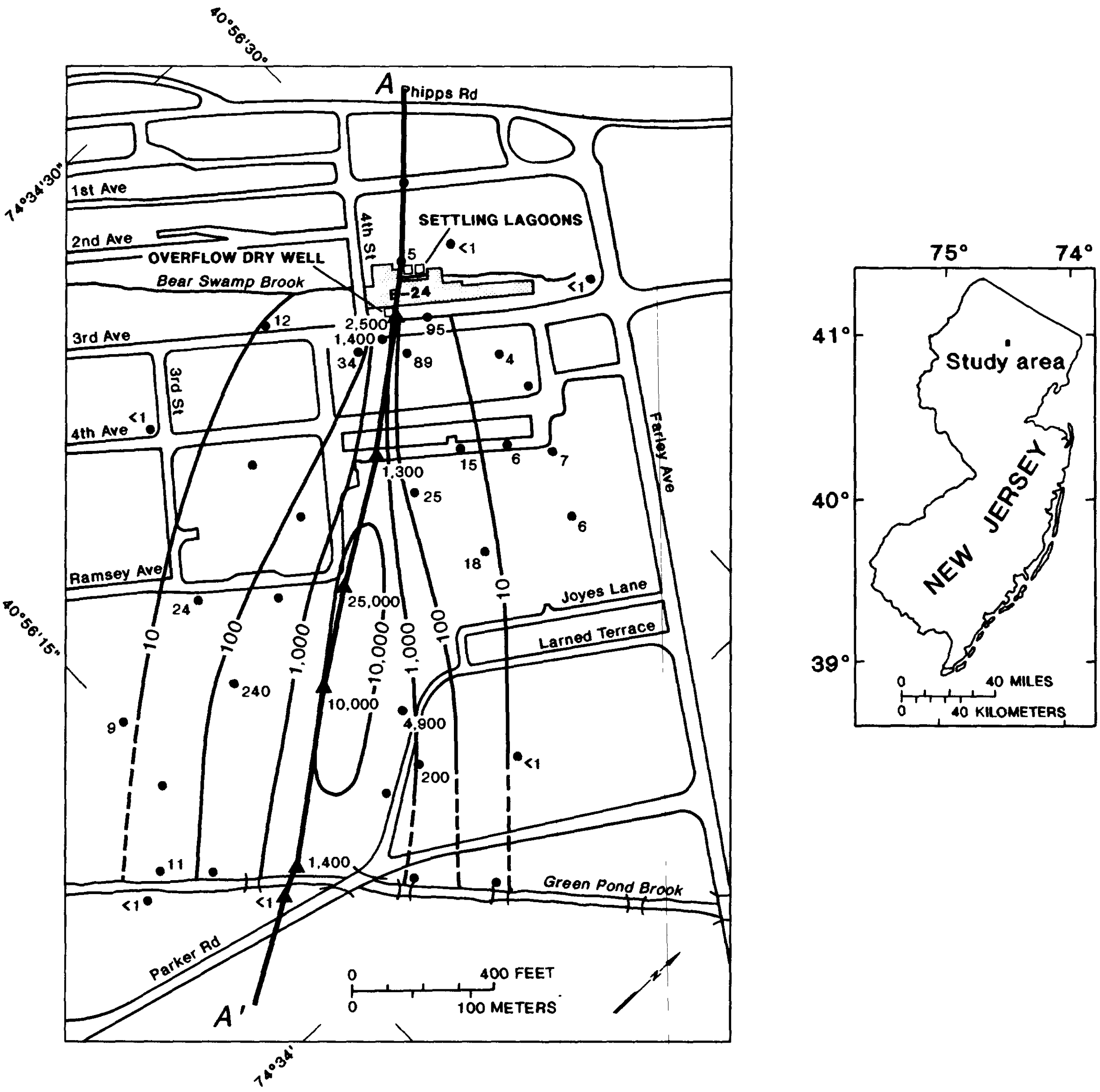

40°56'30"
74°34'30"
40°56'15"
74°34'
A
A'
Phipps Rd
1st Ave
2nd Ave
OVERFLOW DRY WELL
Bear Swamp Brook
SETTLING LAGOONS
4th St
B-24
3rd Ave
3rd St
4th Ave
Ramsey Ave
Farley Ave
Joyes Lane
Larned Terrace
Green Pond Brook
Parker Rd
5
<1
<1
12
2,500
1,400
95
34
89
4
<1
1,300
15
6
7
25
6
18
25,000
24
10
100
1,000
10,000
1,000
100
10
240
10,000
4,900
9
<1
200
1,400
11
<1
<1
0
400 FEET
0
100 METERS
N
75°
74°
41°
40°
39°
Study area
NEW JERSEY
0
40 MILES
0
40 KILOMETERS

EXPLANATION

——10—— LINE OF EQUAL TRICHLOROETHYLENE CONCENTRATION--Shows trichloroethylene concentration, in micrograms per liter. Dashed where approximate.

A——A' Line of section shown in figure 2

18● Well site location and maximum trichloroethylene concentration, in micrograms per liter.

● Well site location not sampled

▲ Well site location and maximum trichloroethylene concentration, in micrograms per liter, with soil-vapor probes

< Less than

Figure 1. Location of Building 24 study area at Picatinny Arsenal, New Jersey; sampling well network; and areal extent of trichloroethylene contaminant plume, November-December 1989.

CHEMICAL EVIDENCE OF PHYSICAL, CHEMICAL, AND BIOLOGICAL PROCESSES

Results of research at other sites contaminated with chlorinated solvents have shown that physical processes, such as advection, dispersion, and nonaqueous-phase flow; chemical processes such as volatilization, sorption, and dissolution; and biological processes such as aerobic and anaerobic biotransformation, can affect the fate and transport of these compounds through an aquifer system (Mackay and others, 1985). The results of chemical analyses of ground-water, soil-gas, and sediment samples collected from the Building 24 site were evaluated to determine whether each of these processes is occurring in the aquifer at the Picatinny Arsenal site.

Physical Processes

The physical processes of advection and dispersion previously have been shown to affect the fate and transport of TCE in the aquifer system at Picatinny Arsenal (Imbrigiotta and others, 1989; Martin, 1989). The plume of TCE generally follows the direction of ground-water flow lines and head gradients as it moves from Building 24, the source, to Green Pond Brook, the ground-water discharge for the aquifer system (figs. 1 and 2).

Nonaqueous-phase flow is hypothesized to have occurred in the system because TCE condensed in the degreaser overflow pipe and discharged directly to the dry well in front of Building 24. This hypothesis is supported by several facts: (1) Pure TCE is a dense nonaqueous-phase liquid (DNAPL) with a specific gravity of 1.47 grams per cubic centimeter at 20 degrees Celsius. Because it is denser than ground water, DNAPL TCE can sink downward through the unconfined aquifer until further movement is restricted by the fine-grained sediments of a confining layer (Mackay and others, 1985); (2) the highest TCE concentrations in the plume (>10,000 μg/L (micrograms per liter)) were found near the base of the unconfined aquifer midway between Building 24 and Green Pond Brook (fig. 2); and (3) preliminary results of solute-transport modeling indicate that these high TCE concentrations are not caused by either a time-dependent (pulse-input) TCE source near Building 24 or a time-dependent (pumpage-affected) flow system.

The highest TCE concentration found near the base of the unconfined aquifer was 25 mg/L (milligrams per liter) (fig. 2), which is significantly less than the 1,100 mg/L TCE saturation concentration that would be expected in the vicinity of DNAPL TCE. The presence of TCE concentrations less than saturation, however, does not invalidate the hypothesis that nonaqueous-phase flow has occurred and that DNAPL TCE exists in the system. Makay and others (1985) have noted that concentrations of TCE can be greatly reduced only a short distance from a pocket of DNAPL TCE as a result of mass-transfer limitations and dispersion. In addition, Sitar and others (1987) reported that TCE concentrations in ground-water samples can be below solubility limits even when soil-extract concentration data indicate the presence of a separate phase.

Chemical Processes

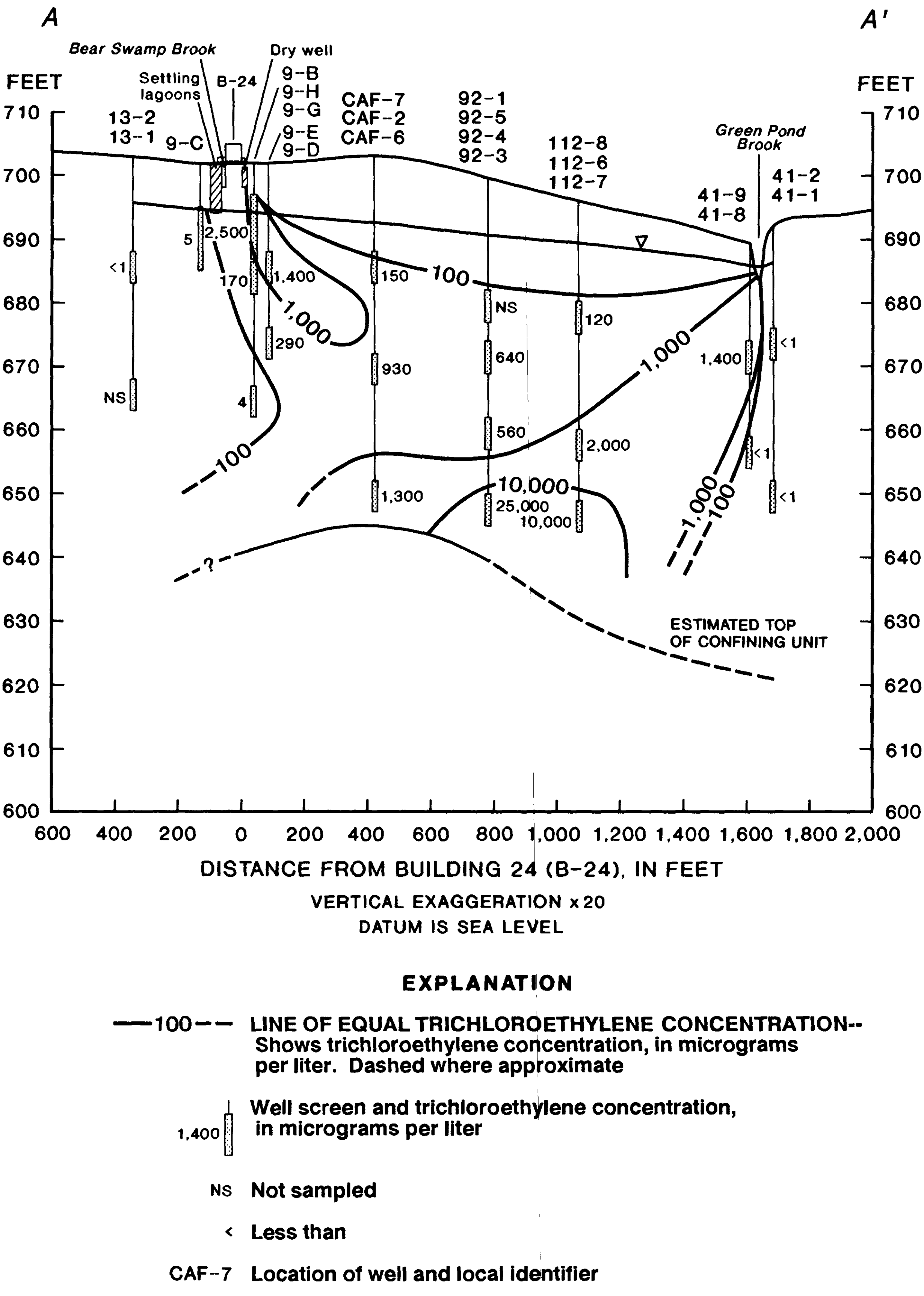
The chemical process of volatilization of TCE from the water table into the unsaturated-zone soil gas above the aquifer at Picatinny Arsenal has been described previously by Smith and others (1990). They found that soil-gas TCE concentrations measured at six sites along the central axis of the contaminant plume generally increased and decreased with the concentrations of TCE measured in shallow ground water. In addition, the concentration of TCE in the soil gas decreased linearly with distance above the water table, suggesting that the transport of TCE in the unsaturated zone is driven principally by molecular diffusion.

Sorption of TCE to aquifer sediments and dissolution of DNAPL TCE also can affect the fate and transport of TCE at Picatinny Arsenal. All inputs of TCE to the ground-water system ceased in 1985, when the overflow pipe to the dry well was capped. If sorption and dissolution do not occur, the TCE concentrations in the ground water, particularly near the source, will decrease significantly as water in the vicinity of Building 24 is flushed out of the aquifer system to Green Pond Brook. This hypothesis is confirmed by preliminary solute-transport simulations in which the TCE source is completely removed. Results of these simulations show that TCE concentrations decrease to less than 10 μg/L in 3 months in well 9-D and in 5 months in well 9-E (both near Building 24) (fig. 2). If desorption of TCE from aquifer sediments or dissolution of DNAPL TCE are occurring, however, then relatively constant concentrations of TCE would be expected to continue to emanate from the source area. TCE concentrations in water from four wells immediately downgradient from Building 24 have decreased only by a factor of 2 or less during the 3-year period from October 1987 to September 1990 (fig. 3). The fact that TCE concentrations near the source have not declined significantly is strong evidence that one or both of these processes are occurring at Picatinny Arsenal.

Sorption of TCE to aquifer sediments can be estimated from the organic-carbon content of the sediments. Organic carbon concentrations measured on 75 aquifer-sediment samples collected in the vicinity of Building 24 and the contaminant plume ranged from less than 0.05 percent to 1.04 percent, with a median concentration of 0.05 percent. Eighty-four percent of the sediment samples contained less than 0.10 percent organic carbon. Low concentrations of sediment organic carbon tend to minimize TCE sorption and decrease the potential for significant slow desorption (Chiou and others, 1983); however, because nearly half of the sediment-organic-carbon values greater than 0.10 percent were measured at sites immediately downgradient from Building 24, this process can be important at the local scale. Higher soil-organic-carbon concentrations have been reported for unsaturated-zone soils above the contaminant plume (Smith and others, 1990).

Biological Processes

The fate and transport of TCE can be affected significantly by both aerobic and anaerobic biotransformation processes. Therefore, the presence or


A
A'
Bear Swamp Brook
Dry well
Settling lagoons
B-24
9-B
9-H
9-G
9-E
9-D
13-2
13-1
9-C
CAF-7
CAF-2
CAF-6
92-1
92-5
92-4
92-3
112-8
112-6
112-7
Green Pond Brook
41-9
41-8
41-2
41-1
FEET
710
700
690
680
670
660
650
640
630
620
610
600
<1
NS
5
2,500
170
4
1,400
290
150
930
1,300
NS
640
560
25,000
10,000
120
2,000
1,400
<1
100
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?
ESTIMATED TOP OF CONFINING UNIT
600 400 200 0 200 400 600 800 1,000 1,200 1,400 1,600 1,800 2,000
DISTANCE FROM BUILDING 24 (B-24), IN FEET
VERTICAL EXAGGERATION x20
DATUM IS SEA LEVEL
EXPLANATION
100
LINE OF EQUAL TRICHLOROETHYLENE CONCENTRATION-- Shows trichloroethylene concentration, in micrograms per liter. Dashed where approximate
1,400
Well screen and trichloroethylene concentration, in micrograms per liter
NS Not sampled
< Less than
CAF-7 Location of well and local identifier

Figure 2. Vertical section showing vertical distribution of trichloroethylene in the contaminant plume in the Building 24 study area at Picatinny Arsenal, New Jersey, November-December 1989. (Location of section A-A' is shown in fig. 1.)

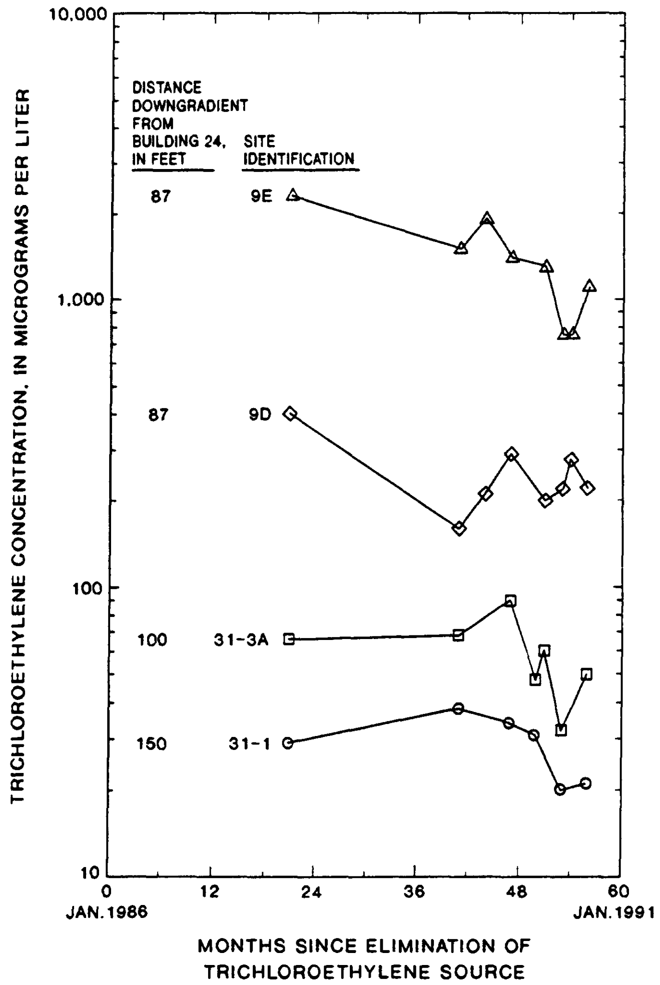


Figure 3. Graph of trichloroethylene concentrations measured from 1987-90 in ground water from four wells immediately downgradient from Building 24.

absence of dissolved oxygen in the ground water determines, in part, which type of biologically-mediated process will occur. A plot of the dissolved-oxygen concentrations measured along section A-A' is shown in figure 4. When plotted on the same section, the TCE plume (fig. 2) coincides almost exactly with the area in which the concentration of dissolved oxygen is less than 0.5 mg/L (anoxic conditions). With few exceptions, this correlation also exists areally.

Under aerobic conditions, TCE is oxidized cometabolically in the laboratory, to acetate and chloride by methane monooxygenase, an enzyme produced by methane-utilizing microorganisms in the presence of methane (Wilson and Wilson, 1985). Aerobic biotransformation of TCE was rapid in soil microcosms amended with methane and containing unsaturated-zone soils collected near the source at Building 24 at Picatinny Arsenal (Ehlke, 1989). Research elsewhere has indicated that this cometabolic process is sensitive to the concentrations of methane, oxygen, TCE, and trace elements (Roberts and others, 1989). Because the TCE plume is primarily anoxic, only 8 of 74 wells at Picatinny Arsenal contain ground water with coexisting detectable concentrations of oxygen, TCE, and methane. Thus, although the overall importance of aerobic TCE biotransformation at this site probably is limited compared to other processes affecting the fate and transport of TCE in the aquifer, a few locations may offer a unique opportunity to study this process under field conditions.

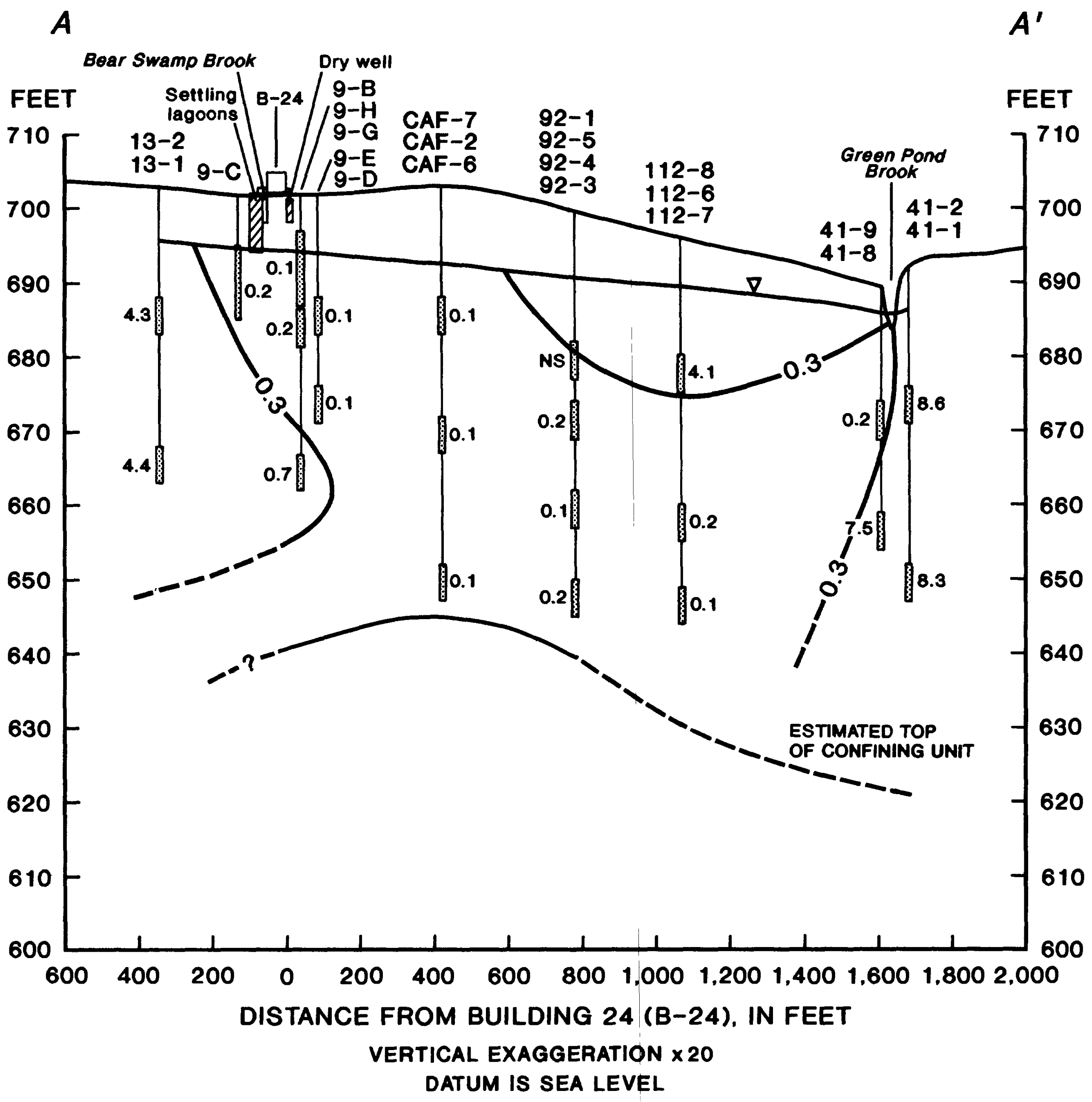
Under anaerobic conditions, TCE has been shown to undergo reductive dehalogenation (the sequential replacement of the chlorine atoms on the molecule with hydrogen atoms) to form three dichloroethylene isomers (primarily cis-1,2-dichloroethylene (cisDCE)) and vinyl chloride (VC) as byproducts: these byproducts are ultimately transformed to carbon dioxide (Parsons and others, 1984; Vogel and others, 1987). Because neither cisDCE nor VC was used at Building 24, their detection in the ground-water plume indicates that reductive dehalogenation of TCE is occurring in the aquifer. The anaerobic and reducing conditions required for this process are present throughout much of the TCE plume. Results of analyses of ground water samples collected in November-December 1989 indicate that cisDCE and VC were detected in water from 40 and 18 of the 53 wells in which TCE was detected, respectively. Thus, reductive dehalogenation is occurring in 75 percent of the wells in the Building 24 plume and probably is the dominant biological process affecting the fate and transport of TCE at Picatinny Arsenal.

The availability of alternate electron acceptors for microorganisms to utilize in the absence of oxygen also can influence the occurrence of reductive dehalogenation. Nitrate, sulfate, and bicarbonate or carbon dioxide are used as electron acceptors as conditions become progressively more reducing (Vogel and others, 1987); therefore, the occurrence of other biogenic reductive processes, such as nitrate reduction, sulfate reduction, and methanogenesis, can affect the activity of the reductive dehalogenation of TCE at a site.

Of the above-mentioned processes, only methanogenesis (the production of methane by oxidation of organic acids or carbon dioxide) has been studied in detail at Picatinny Arsenal. The occurrence of methanogenesis at the site, is evidenced by the detection of dissolved methane in concentrations ranging from 1 µg/L to 1,200 µg/L in 73 percent of the water samples collected during November-December 1989. Along the central axis of the plume, higher concentrations of methane (fig. 5) generally coincide with the location of the anaerobic TCE plume (figs. 2 and 4). Detectable concentrations of methane (≥1 µg/L) were found in 85 percent of the wells containing cisDCE and in 94 percent of the wells containing VC. The simultaneous occurrence of reductive dehalogenation of TCE and methanogenesis has been reported previously in laboratory studies, but the biochemical relation between these two processes in the field has not been determined (Fathepure and Boyd, 1988; Baek and Jaffe, 1989). Results of the laboratory studies suggest that methanogenesis may function as a source of the reduced electron carriers necessary to facilitate the reductive dehalogenation of TCE (Baek and Jaffe, 1989).

CONCLUSIONS

Results of chemical analyses of ground water, soil gas, and aquifer sediments from a contaminant plume near Building 24 at Picatinny Arsenal, N.J., suggest that the fate and transport of chlorinated solvents, particularly TCE, are


A
A'
Bear Swamp Brook
Dry well
Settling lagoons
B-24
9-B
9-H
9-G
9-E
9-D
9-C
13-2
13-1
CAF-7
CAF-2
CAF-6
92-1
92-5
92-4
92-3
112-8
112-6
112-7
Green Pond Brook
41-9
41-8
41-2
41-1
FEET
710
700
690
680
670
660
650
640
630
620
610
600
4.3
4.4
0.1
0.2
0.2
0.7
0.1
0.1
0.1
0.1
0.1
NS
0.2
0.1
0.2
4.1
0.2
0.1
0.3
0.3
0.3
0.2
7.5
8.6
8.3
?
ESTIMATED TOP OF CONFINING UNIT
600
400
200
0
200
400
600
800
1,000
1,200
1,400
1,600
1,800
2,000
DISTANCE FROM BUILDING 24 (B-24), IN FEET
VERTICAL EXAGGERATION x20
DATUM IS SEA LEVEL

EXPLANATION

——0.3—— **LINE OF EQUAL DISSOLVED-OXYGEN CONCENTRATION--Shows dissolved-oxygen concentration, in milligrams per liter. Dashed where approximate**

0.2 ▯ **Well screen and dissolved-oxygen concentration, in milligrams per liter**

NS **Not sampled**

CAF-7 **Location of well and local identifier**

Figure 4. Vertical section showing vertical distribution of dissolved-oxygen concentrations in the Building 24 area, November-December 1989. (Location of section A-A' is shown in fig. 1.)

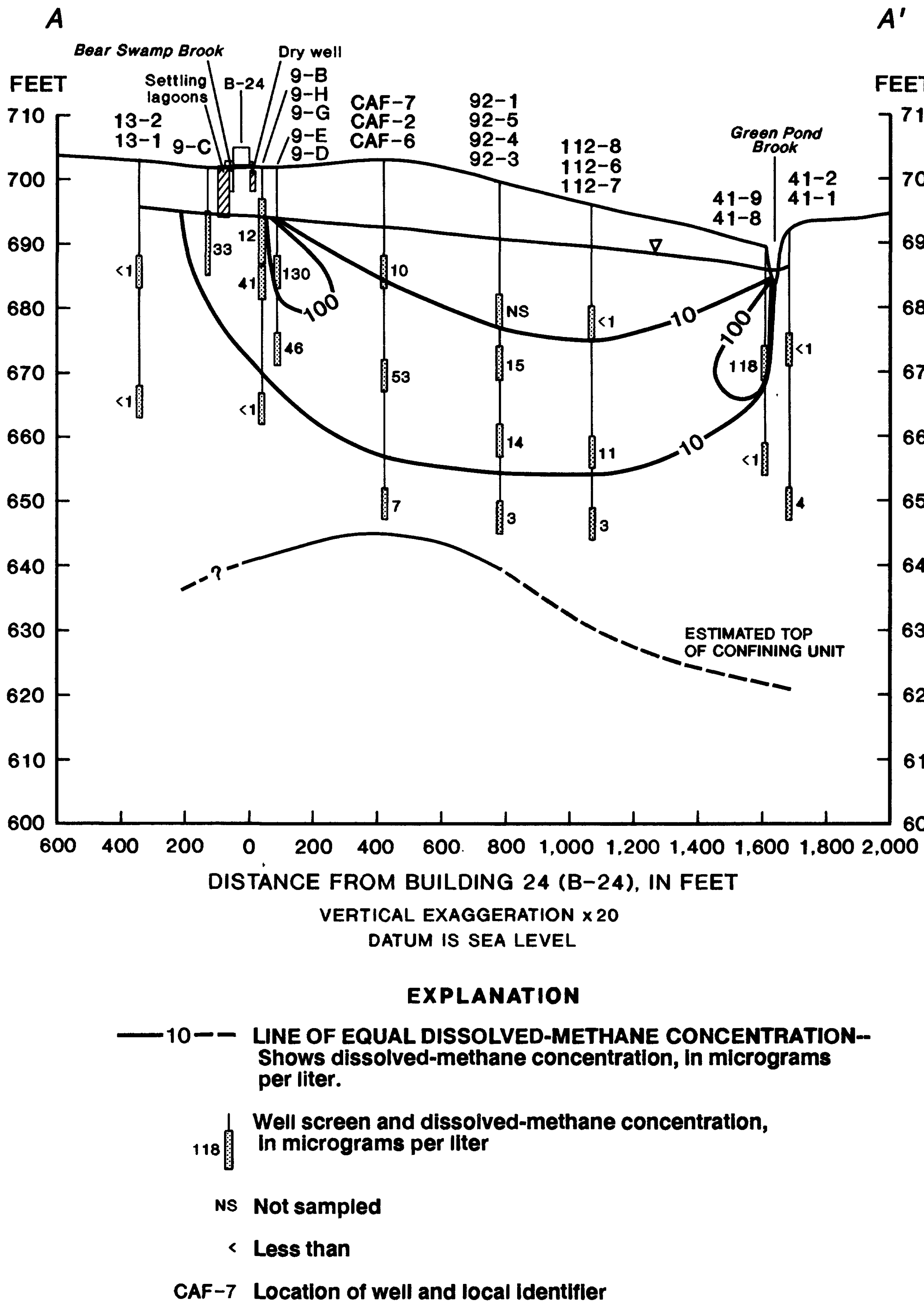


Figure 5. Vertical section showing vertical distribution of dissolved-methane concentrations in the Building 24 area, November-December 1989. (Location of section A-A' is shown in fig. 1.)

affected by physical, chemical, and biological processes at this site. The TCE plume moves advectively from the source area to Green Pond Brook, following the direction of ground-water flow lines and head gradients. Nonaqueous-phase flow of TCE is supported by high TCE concentrations near the base of the unconfined aquifer and preliminary results of solute-transport modeling. Volatilization of TCE to the unsaturated-zone soil gas was measured and transport in the unsaturated zone was determined to be driven principally by molecular diffusion. Relatively constant TCE concentrations near the source from 1987 to 1990 suggest the occurrence of slow desorption of TCE from contaminated aquifer sediments and(or) dissolution of DNAPL TCE in the aquifer. The detection of cis DCE and VC in 75 percent of the wells in the plume is indicative of biologically-mediated reductive dehalogenation of TCE. Evidence of methanogenesis was found in 85 percent of the wells in which cisDCE was detected and in 94 percent of the wells in which VC was detected.

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BIOTRANSFORMATION OF CIS-1,2-DICHLOROETHYLENE IN AQUIFER MATERIAL FROM PICATINNY ARSENAL, MORRIS COUNTY, NEW JERSEY

By Theodore A. Ehlke [1], Thomas E. Imbrigiotta [1], Barbara H. Wilson [2], *and* John T. Wilson [3]

ABSTRACT

Soil cores were collected within and adjacent to a trichloroethylene plume that has contaminated the shallow aquifer at Picatinny Arsenal, New Jersey, to study the rate of cis-1,2-dichloroethylene biotransformation. Soil cores also were collected at a highly contaminated site within the plume to determine the effect of different electron donors on the rate of cis-1,2-dichloroethylene biotransformation under methanogenic conditions. Ground-water samples were analyzed for volatile organic compounds to study the relation between volatile-organic-compound concentrations and the biotransformation of cis-1,2-dichloroethylene. Biotransformation in microcosms from sites within the plume ranged from slight to more than 90 percent after an incubation period of 32 weeks. The most extensive biotransformation in soil microcosms occurred at a site near the highest in situ cis-1,2-dichloroethylene concentration measured at the arsenal (710 micrograms per liter). Biotransformation was negligible at an uncontaminated site. Amendment of soil microcosms with combinations of methanol, formate, toluene, p-cresol, propionate, and butyrate inhibited the biotransformation of cis-1,2-dichloroethylene. A combination of methanol and formate had the greatest inhibitory effect.

INTRODUCTION

Cis-1,2-dichloroethylene (cis-1,2-DCE) is commonly found in ground water that also contains trichlorethylene (TCE), tetrachloroethylene (PCE), or 1,1,1-trichloroethane (TCA). TCA can undergo abiotic transformation to 1,1-dichloroethylene (1,1-DCE) in soil (Vogel and McCarty, 1985; 1987). More commonly, cis- and trans-1,2-dichloroethylene are formed by reductive dehalogenation of PCE and TCE under methanogenic conditions by anaerobic soil microorganisms. Cis-1,2-DCE is by far the most common of the three DCE isomers in ground water at Picatinny Arsenal, N.J., where it ranges in concentration from less than 1 µg/L (microgram per liter) to 710 µg/L (fig. 1). Cis-1,2-DCE is a mutagen with a maximum allowable concentration in drinking water of 10 µg/L (New Jersey Department of Environmental Protection, 1989).

All chlorinated ethylenes are biotransformed in soil by reductive dehalogenation under methanogenic conditions to vinyl chloride (VC), a carcinogen, and ultimately to carbon dioxide (CO_2) and chloride, as shown in fig. 2. The rate of reductive dehalogenation generally decreases with decreasing number of attached chlorines; thus, the anaerobic biotransformation of TCE in soil reportedly occurs more rapidly than that of DCE or VC (Fathepure and Boyd, 1988, p. 2976). The placement of chlorine atoms on the carbon molecule also affects the rate of dechlorination. Results of tracer studies conducted by Roberts and others (1989, p. 57) indicate that the apparent transport velocity of cis- and trans-1,2-DCE in saturated parts of the aquifer is about twice that of TCE, and half that of VC. Thus, the maximum aqueous concentrations of TCE, cis-1,2-DCE, and VC in typical contaminant plumes are expected to be spatially distinct as the contaminants are transported downgradient.

Many biogeochemical factors control the rate of *in situ* biotransformation of TCE, cis-1,2-DCE, and VC. Substrate concentration, availability and type of electron donor and acceptor, concentration of cocontaminants, and other biogenic processes such as methanogenesis are reported to affect the rate of microbial degradation of chlorinated organic compounds (Fathepure and Boyd, 1988; Baek and Jaffé, 1989; Freedman and Gossett, 1989).

A release of TCE from 1960 to 1981 at a metal-plating and degreasing facility in Building 24 at Picatinny Arsenal has resulted in a 1,600-ft(foot)-long contaminant plume between Building 24 and Green Pond Brook (fig. 3), which has contaminated the shallow aquifer to a depth of at least 100 ft. The major organic contaminants within the plume are TCE, cis- and trans-1,2-DCE, VC, TCA, and PCE (Sargent and others, 1986, p. 1). In 1989, the maximum concentrations in ground water at the arsenal of TCE, cis-1,2-DCE, and VC were 25,000, 710, and 31 µg/L, respectively. The presence of cis-1,2-DCE and VC in ground water indicates that reductive dehalogenation of TCE has occurred in the shallow aquifer.

The purpose of this paper is to estimate the rate of *in situ* biotransformation of cis-1,2-DCE in the shallow aquifer at Picatinny Arsenal at locations within the TCE plume and at an uncontaminated site as determined from laboratory microcosm studies. This report also compares the biotransformation of cis-1,2-DCE as measured in the laboratory to TCE, VC, and cis-1,2-DCE concentrations in ground water at various locations. The effect of a series of cosubstrates (electron donors) on the rate of cis-1,2-DCE biotransformation in the laboratory under methanogenic conditions also is described.

METHODS

Results of previous studies conducted at Picatinny Arsenal (Sargent and others, 1986; 1990) indicate that concentrations of TCE, cis-1,2-DCE, and VC in ground water vary greatly not only within the plume (figs. 1 and 3), but also with depth (fig. 4). The TCE concentration in ground water exceeded 10 mg/L (milligrams per liter) at the top of the water table near Building 24 and declined to less than 1 mg/L at the base of the shallow aquifer near the contaminant source. Downgradient from the contaminant source, the concentrations of TCE and cis-1,2-DCE generally increased with depth, except at wells near Green

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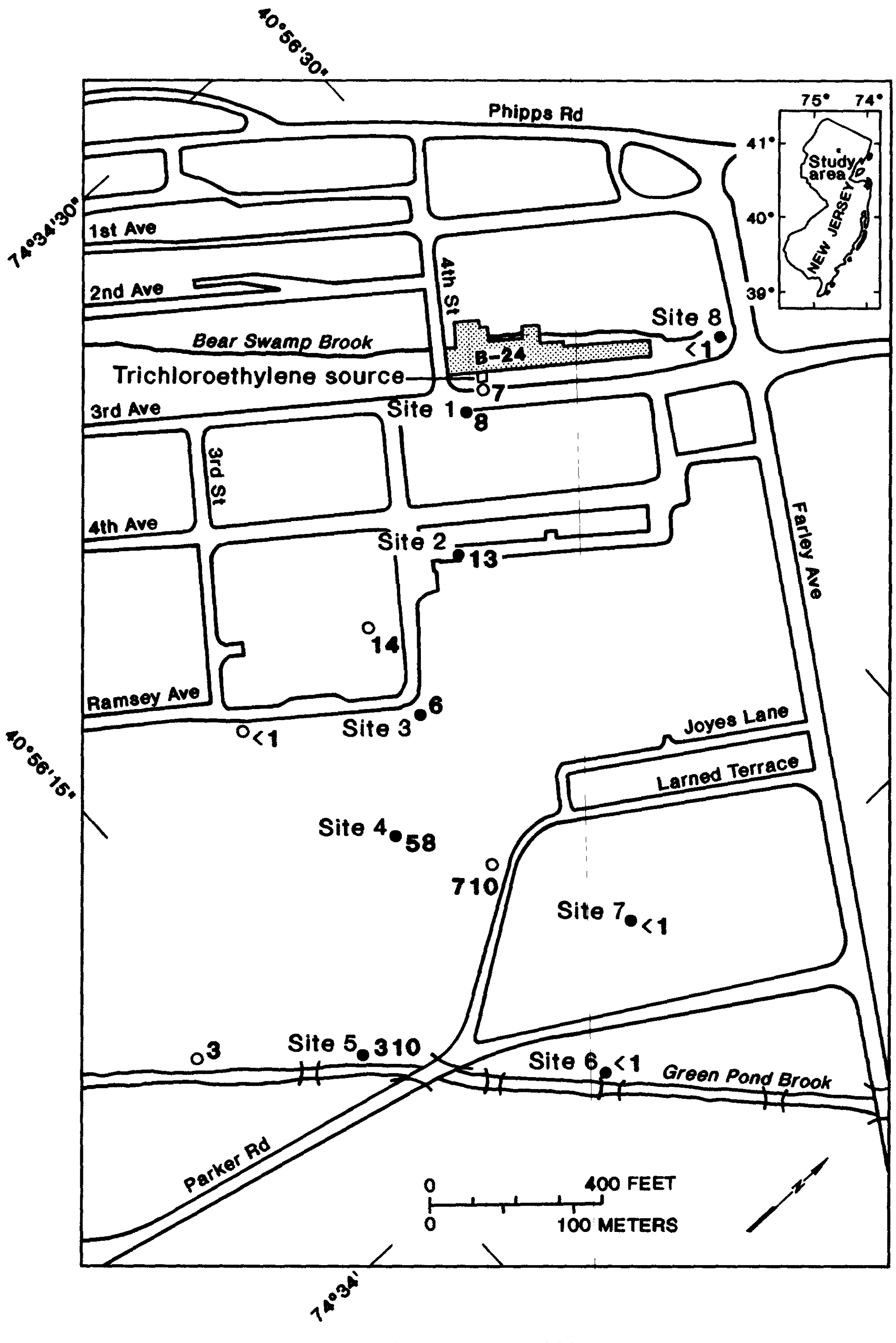
40°56'30"
Phipps Rd
75°
74°
41°
40°
39°
Study area
NEW JERSEY
74°34'30"
1st Ave
2nd Ave
4th St
Bear Swamp Brook
Site 8
<1
B-24
Trichloroethylene source
7
3rd Ave
Site 1
8
3rd St
4th Ave
Site 2
13
Farley Ave
14
Ramsey Ave
<1
Site 3
6
Joyes Lane
40°56'15"
Larned Terrace
Site 4
58
710
Site 7
<1
3
Site 5
310
Site 6
<1
Green Pond Brook
Parker Rd
0
400 FEET
0
100 METERS
74°34'

EXPLANATION

Site 8 <1● Soil-core-collection site, identification number, and concentration of cis-1,2-dichloroethylene, in micrograms per liter. Concentrations are shown for depth at which soil cores were collected, where appropriate

○3 Well location and concentration of cis-1,2-dichloroethylene, in micrograms per liter

Figure 1. Concentration of cis-1,2-dichloroethylene in observation wells at Picatinny Arsenal, New Jersey, during 1989.

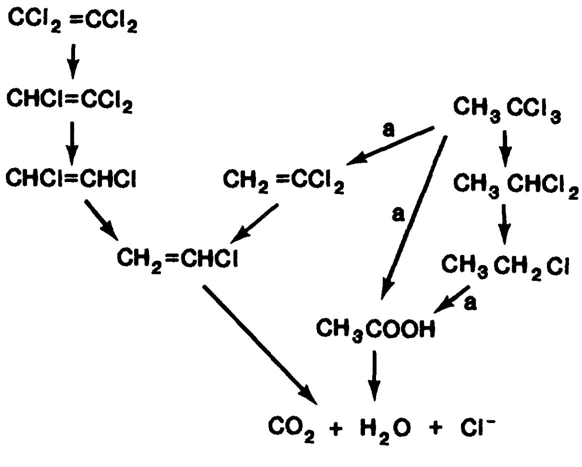

Figure 2. Anaerobic transformation pathways for selected chlorinated aliphatic compounds. (Modified from Vogel and others, 1987.) (Arrows with "a" indicate abiotic transformations, other arrows represent biotic transformations.)

Pond Brook, where they decreased. In order to test the hypothesis that observed differences in concentrations of cis-1,2-DCE and VC in ground water reflect real differences in *in situ* biotransformation rates of cis-1,2-DCE, soil cores were collected at five locations along the longitudinal axis of the plume at Picatinny Arsenal and at three sites outside the plume, as shown in fig. 1. Site 6, which is located near Green Pond Brook and is not contaminated with TCE, VC, or cis-1,2-DCE, was chosen as a control site.

Collection of Core Samples

Drilling and soil-core-handling techniques were chosen to minimize the possibility of soil-sample contamination during drilling. Soil cores were collected at selected depths in the shallow aquifer near the vertical center of the TCE plume, determined from a previous study (Sargent and others, 1990). Core holes were drilled to the desired sampling depth with a 10-in. (inch)-outside-diameter by 6-in.-inside-diameter hollow-stem auger. Soil cores were obtained by using a 4-in.-inside-diameter piston coring device which retained the soil and fluids. Soil cores were extruded hydraulically from the core barrel in an anaerobic field glove box into sterilized 1-quart glass Mason[4] jars after the exposed outer 0.5 in. of core material was pared away aseptically as previously described (Wilson and others, 1983; Leach and others, 1988). Soil-core samples were stored on ice in a cooler while enroute to the laboratory and were refrigerated at 4 °C (degrees Celsius) thereafter until used for laboratory microcosm setup. Water samples were collected from wells at the same location as the soil cores to determine *in situ* chemical conditions at the time of soil-core collection. Chemical results are summarized elsewhere in this paper and are discussed in greater detail in other papers in this Proceedings.

Laboratory Microcosm Study

The biotransformation of cis-1,2-DCE at sites shown in figure 1 was studied in laboratory soil microcosms under methanogenic conditions. Fifty-mL (milliliter) (actual volume, 60 mL) serum bottles were filled to the neck with 110 grams of a well-mixed soil slurry in an anaerobic chamber. The serum bottles were next amended with 3 mL of a sterilized cis-1,2-DCE solution to give an initial aqueous cis-1,2-DCE concentration of approximately 11.3 µmol (micromoles) (1,100 µg/L).

Anaerobic biotransformation of chlorinated ethylenes such as PCE, TCE, DCE, and VC is affected by the availability of a suitable electron donor to sustain the reductive dechlorination process. Freedman and Gossett (1989) studied the effect of amendment with a series of electron donors on the biotransformation of PCE and TCE. Methanol effectively sustained dechlorination, as did hydrogen, formate, acetate, and glucose. The ground water at Picatinny Arsenal contains many cocontaminants, such as toluene, which might serve as auxiliary electron donors and thus affect the rate of *in situ* biotransformation of TCE, DCE, and VC in the study area. Biotransformation of cis-1,2-DCE at site 4 (fig. 1), where active dechlorination of cis-1,2-DCE was believed to occur, was studied by using three combinations of auxiliary electron donors, as shown in table 1. The cis-1,2-DCE concentration in ground water at

Table 1. Concentration and type of electron donor used to study biotransformation of cis-1,2-dichloroethylene at site 4 at Picatinny Arsenal, New Jersey

[Cis-1,2-DCE, cis-1,2-dichloroethylene; µmol, micromole; mmol, millimole; site location shown in fig. 1].

Treatment	Concentration
Cis-1,2-DCE	11.3 µmol
Cis-1,2-DCE	11.3 µmol
Sodium formate	1 mmol
Methanol	1 mmol
Cis-1,2-DCE	11.3 µmol
Toluene	0.1 mmol
p-cresol	0.1 mmol
Sodium propionate	0.1 mmol
Sodium butyrate	.1 mmol
Sodium formate	1 mmol
Cis-1,2-DCE	11.3 µmol
Toluene	0.1 mmol
p-cresol	0.1 mmol
Sodium propionate	0.1 mmol
Sodium butyrate	0.1 mmol

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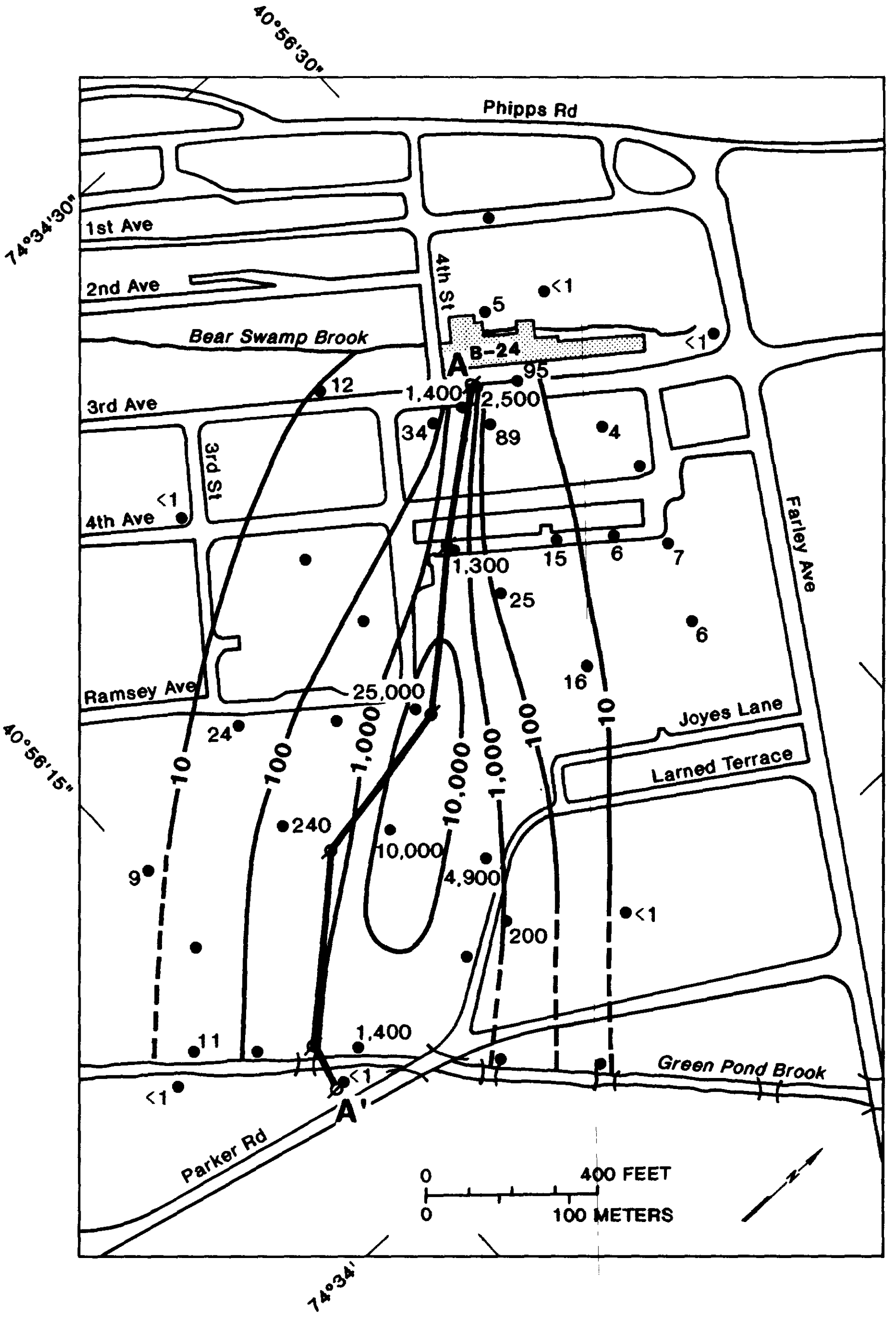
[4] The use of brand, firm, or trade names in this paper is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.


40°56'30"
74°34'30"
40°56'15"
74°34'
Phipps Rd
1st Ave
2nd Ave
Bear Swamp Brook
3rd Ave
4th Ave
Ramsey Ave
3rd St
4th St
Farley Ave
Joyes Lane
Larned Terrace
Green Pond Brook
Parker Rd
B-24
A
A'
<1
5
95
1,400
2,500
34
89
4
12
1,300
15
6
7
25
6
16
25,000
24
240
10,000
4,900
9
200
<1
1,400
11
<1
<1
10
100
1,000
10,000
1,000
100
10
0
400 FEET
0
100 METERS
N

EXPLANATION

—10— — TRICHLOROETHYLENE-CONCENTRATION CONTOUR--Shows trichloroethylene concentration, in micrograms per liter. Dashed where approximate.

A⌀——⌀A' LINE OF HYDROGEOLOGIC SECTION SHOWN IN FIGURE 4

● 6 Well location and trichloroethylene concentration, in micrograms per liter

⌀ Drive-point site

Figure 3. Concentration of trichloroethylene in observation wells at Picatinny Arsenal, New Jersey, during 1989.

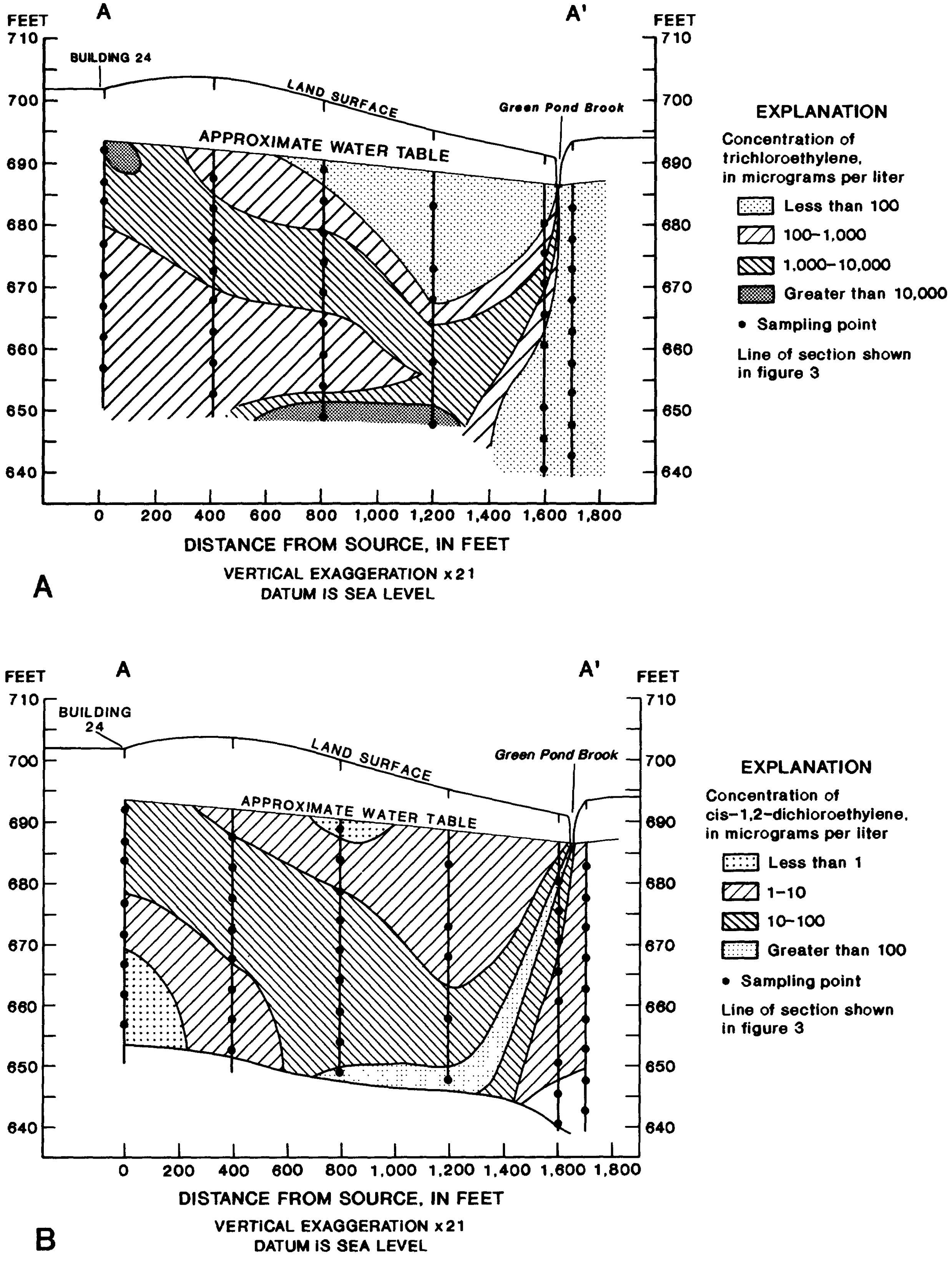

FEET
A
A'
FEET
710
700
690
680
670
660
650
640
BUILDING 24
LAND SURFACE
Green Pond Brook
APPROXIMATE WATER TABLE
0
200
400
600
800
1,000
1,200
1,400
1,600
1,800
DISTANCE FROM SOURCE, IN FEET
VERTICAL EXAGGERATION x21
DATUM IS SEA LEVEL
A
EXPLANATION
Concentration of trichloroethylene, in micrograms per liter
Less than 100
100–1,000
1,000–10,000
Greater than 10,000
• Sampling point
Line of section shown in figure 3
FEET
A
A'
FEET
710
700
690
680
670
660
650
640
BUILDING 24
LAND SURFACE
Green Pond Brook
APPROXIMATE WATER TABLE
0
200
400
600
800
1,000
1,200
1,400
1,600
1,800
DISTANCE FROM SOURCE, IN FEET
VERTICAL EXAGGERATION x21
DATUM IS SEA LEVEL
B
EXPLANATION
Concentration of cis-1,2-dichloroethylene, in micrograms per liter
Less than 1
1–10
10–100
Greater than 100
• Sampling point
Line of section shown in figure 3

Figure 4. Areal distribution of (A) trichloroethylene and (B) cis-1,2-dichloroethylene in ground water at Picatinny Arsenal, New Jersey. (Modified from Sargent and others, 1990.)

site 4 at various depths ranged from less than 1 µg/L to 58 µg/L during 1989 (fig. 1). The soil core at this site was collected from the same depth as the highest measured cis-1,2-DCE concentration (58 µg/L). Although it was not added as an amendment, TCE contained in the pore fluid and sorbed to the soil was present in concentrations ranging from less than 1 µg/L to 104 µg/L in microcosm bottles. The microcosms were constructed with a small headspace (about 3 mL) to permit headspace-gas analysis, and were sealed with gray Teflon-faced butyl-rubber septa with aluminum-crimp seals. Microcosm bottles were incubated inverted in darkness at 18 °C, the average *in situ* temperature, after they were filled with soil and dosed with amendments. Controls were autoclaved for 1 hour at 121 °C prior to amendment with cis-1,2-DCE.

The serum bottles were periodically sacrificed at time intervals of 1, 2, 4, 8, 18, and 32 weeks in triplicate to determine the aqueous concentration of cis-1,2-DCE and other volatile organic compounds, headspace-gas composition, viable microbial population, and other physical and chemical variables. Concentrations of volatile organic compounds were quantified by gas chromatography using a modification of U.S. Environmental Protection Agency method 502.2 (U.S. Environmental Protection Agency, 1982).

BIOTRANSFORMATION OF CIS-1,2-DICHLOROETHYLENE IN AQUIFER MATERIAL

Trichloroethylene and Cis-1,2-DCE Concentrations in Ground Water

The results of laboratory analyses of ground-water samples collected at Picatinny Arsenal in 1989 for TCE and cis-1,2-DCE are summarized in figures 3 and 1, respectively. The concentration of TCE ranged from less than 1 to 25,000 µg/L and was highest at site 3 (fig. 3), about midway between the source (Building 24) and the ground-water-discharge point, Green Pond Brook. The maximum TCE concentration in ground water at site 3 is not significantly different from concentrations measured in 1987 and earlier (Sargent and others, 1990).

The concentration of cis-1,2-DCE in ground water in 1989 ranged from less than 0.2 to 710 µg/L (fig. 1). The maximum observed concentration of cis-1,2-DCE (710 µg/L) was in a well near site 4. Relatively high cis-1,2-DCE concentrations also were observed at site 5 (310 µg/L) and site 3 (220 µg/L); however, the soil core at site 3 was collected at a depth where the cis-1,2-DCE concentration was lower (6 µg/L). Lower concentrations of cis-1,2-DCE, ranging from less than 0.2 to 58 µg/L, also were measured at site 4. As predicted by Roberts and others (1989), the maximum concentrations of cis-1,2-DCE and TCE in ground water within the plume were found at wells spatially distinct from each other. The maximum concentration of VC in ground water at the Arsenal in 1989 (31 µg/L) also was found in a well near site 4. Concentrations of VC near Building 24 were lower (23 µg/L).

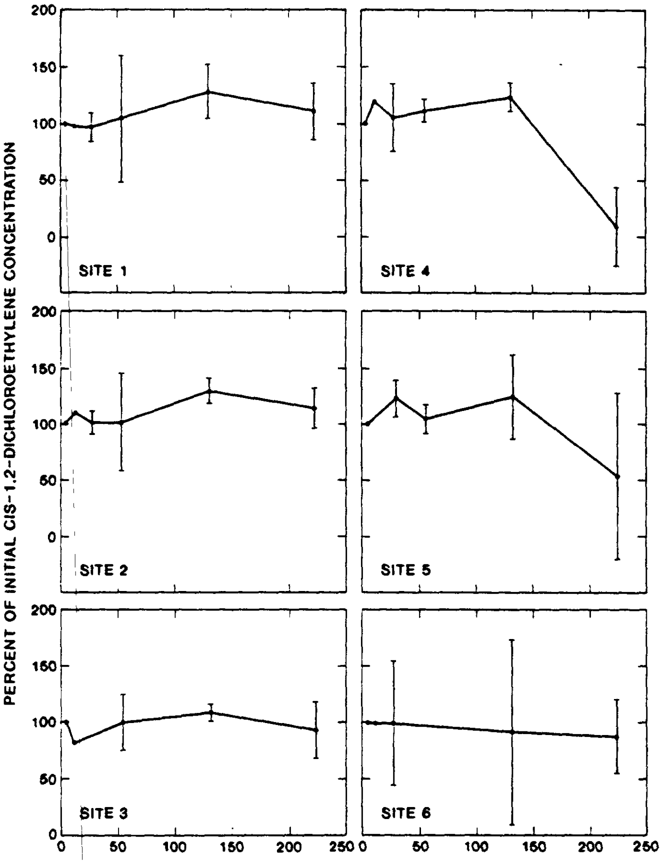


Figure 5. Percent change in concentration of cis-1,2-dichloroethylene in soil micorcosms from sites 1 through 6 at Picatinny Arsenal, New Jersey, at various time intervals. Error bars represent standard error of the mean.

Biotransformation of Cis-1,2-DCE

After a period of acclimation of 8 weeks, the concentration of cis-1,2-DCE increased in all microcosms constructed with soil from within the contaminant plume (fig. 5). Most likely this is a result of reductive dehalogenation of TCE that was sorbed to the soil or present in the pore fluid used to construct the microcosms, forming cis-1,2-DCE. Microbial reductive dehalogenation of cis-1,2-DCE to VC and CO_2 occurs at a slower rate than dehalogenation of TCE to DCE, causing a temporary increase in the concentration of cis-1,2-DCE in soils undergoing anaerobic TCE degradation (Fathepure and Boyd, 1988). The initial increase in cis-1,2-DCE concentration was absent at site 6 (which was not contaminated with TCE or cis-1,2-DCE), as shown in figures 1 and 3.

The aqueous concentration of cis-1,2-DCE increased in the microcosms that were constructed with soil from within the contaminant plume (sites 1-5) during the initial

18-week incubation period, then declined. After 32 weeks of incubation, soil microcosms from the sites near the high in situ cis-1,2-DCE concentrations (sites 4 and 5) showed the greatest percentage of removal of cis-1,2-DCE. Site 4, which was near the well that contained the highest *in situ* concentration of cis-1,2-DCE (710 µg/L), also showed the greatest removal of cis-1,2-DCE, 94 percent after 32 weeks. More than half (55 percent) of the initial cis-1,2-DCE concentration was removed in microcosms constructed with soil from site 5, which had an *in situ* cis-1,2-DCE concentration of 310 µg/L. Removal of cis-1,2-DCE was less at most other sites from 18 to 32 weeks, but may have been underestimated because of concomitant formation of cis-1,2-DCE from TCE that was sorbed to contaminated soil. Slight losses of cis-1,2-DCE (13 percent) in microcosms constructed with uncontaminated soil from site 6 indicates abiotic removal processes, leakage, or slow sorption to glass and soil.

Small concentrations of VC, ranging from less than 0.2 to 2.1 µg/L, were produced in soil microcosms constructed with contaminated soil during the study. The highest concentration of VC (2.1 µg/L) was produced in microcosms constructed with soil from site 5. Analysis of ground-water samples collected at the Arsenal during 1989 indicates that VC concentrations ranged from less than 0.2 µg/L to 31 µg/L, suggesting that extensive biotransformation of TCE and cis-1,2-DCE has occurred at the arsenal and that the observed maximum *in situ* concentration of cis-1,2-DCE (710 µg/L) probably is less than the actual maximum concentration.

Microbial populations in ground water and in soil used to construct the microcosms did not vary significantly at sites 1 through 6. Viable microorganism densities in soil ranged from 1.5×10^5 to 4.7×10^6 per gram of soil. Total microorganisms in ground water, which were determined by acridine orange direct count, ranged from 2.2×10^6 to 2.3×10^7 per mL.

The rate of removal of cis-1,2-DCE in soil microcosms over the 32-week study was affected by the length of the initial lag period, production of cis-1,2-DCE resulting from dechlorination of TCE initially present, and desorption of sorbed cis-1,2-DCE. Apparent cis-1,2-DCE removal, particularly at sites nearest the contamination source, probably was significantly underestimated because of biotransformation of TCE that was sorbed to soil used to construct the microcosms. Biotransformation of cis-1,2-DCE under methanogenic conditions approximately follows first-order rate kinetics (Barrio-Lage and others, 1986). The rate of cis-1,2-DCE removal can be estimated as follows:

$$\text{Removal rate} = \frac{\text{Ln}\left(\dfrac{\text{Initial concentration of cis–1,2–DCE}}{\text{Final concentration of cis–1,2–DCE}}\right)}{\text{Time interval (weeks)}}$$

If cis-1,2-DCE concentration values for weeks 18 through 32 are used to compute a removal rate, the effect of the lag period is excluded for computation purposes. When data for weeks 18 through 32 are used to compute biotransformation rates, the rate of removal is much greater than it would be if data for the entire study interval were used. This method of computation tends to eliminate most of the error resulting from TCE biotransformation (which forms cis-1,2-DCE) and is a more realistic estimate of *in situ* cis-1,2-DCE dechlorination. In this case, the removal rate of cis-1,2-DCE for weeks 18 through 32 for sites 1 through 6 was approximately 0.01, 0.01, 0.01, 0.18, 0.06, and 0.005 per week, respectively (table 2). The rate of cis-1,2-DCE biotransformation was most rapid at site 4 (0.18 per week), where the *in situ* TCE and cis-1,2-DCE concentrations nearest the depth from which soil-core samples were collected were 2,000 and 58 µg/L, respectively, as shown in table 2. The removal of cis-1,2-DCE in muck from the Florida Everglades ranged from 0.01 to 0.06 per week (Barrio-Lage and others, 1986). *In-situ* removal of cis-1,2-DCE by soil microorganisms at Picatinny Arsenal was significantly faster at sites 4 and 5 than at sites 1 through 3 (and at site 6, where the soil was not contaminated with TCE or cis-1,2-DCE). Measured *in situ* concentrations of VC (table 2) and VC concentrations measured in microcosms are not in agreement with stoichometric conversion of cis-1,2-DCE to VC. High, and commonly transient, *in situ* concentrations of VC within the plume at the arsenal may reflect active biotransformation at more distant locations, and subsequent transport downgradient.

Table 2. Comparison of *in situ* trichloroethylene, cis-1,2-dichloroethylene, and vinyl chloride concentrations with computed cis-1,2-dichloroethylene biotransformation rates at Picatinny Arsenal, New Jersey

[Concentrations shown are for the screened interval closest to that at which soil cores were collected; TCE, trichloroethylene; Cis-1,2-DCE, cis-1,2-dichloroethylene; VC, vinyl chloride; <, less than; µg/L, micrograms per liter]

Site	TCE, µg/L (11/89)	Cis-1,2-DCE µg/L (11/89)	VC, µg/L (11/89)	Cis-1,2-DCE biotransformation rate, per week
1	290	8	<1	0.01
2	930	13	2	.01
3	560	6	<1	.01
4	2,000	58	<1	.18
5	1,400	310	6	.06
6	<1	<1	<1	.005

Effect of Electron Donor

The removal of cis-1,2-DCE was greatest in soil microcosms from site 4 that were amended with cis-1,2-DCE only, as shown in figure 6. After 32 weeks, 94 percent of the initial concentration of cis-1,2-DCE was removed in those microcosms. Amendment of similar microcosms with cis-1,2-DCE, toluene, p-cresol, propionate, and butyrate, as shown in table 1, resulted in a 73-percent removal of the initial cis-1,2-DCE concentration after 32 weeks. Amendment with cis-1,2-DCE, toluene, p-cresol, propionate, butyrate, and formate resulted in a 55-percent removal of the cis-1,2-DCE during the same period. The addition of cis-1,2-DCE plus methanol and formate resulted in the least removal of cis-1,2-DCE (5 percent) after 32 weeks. These findings contradict the report that

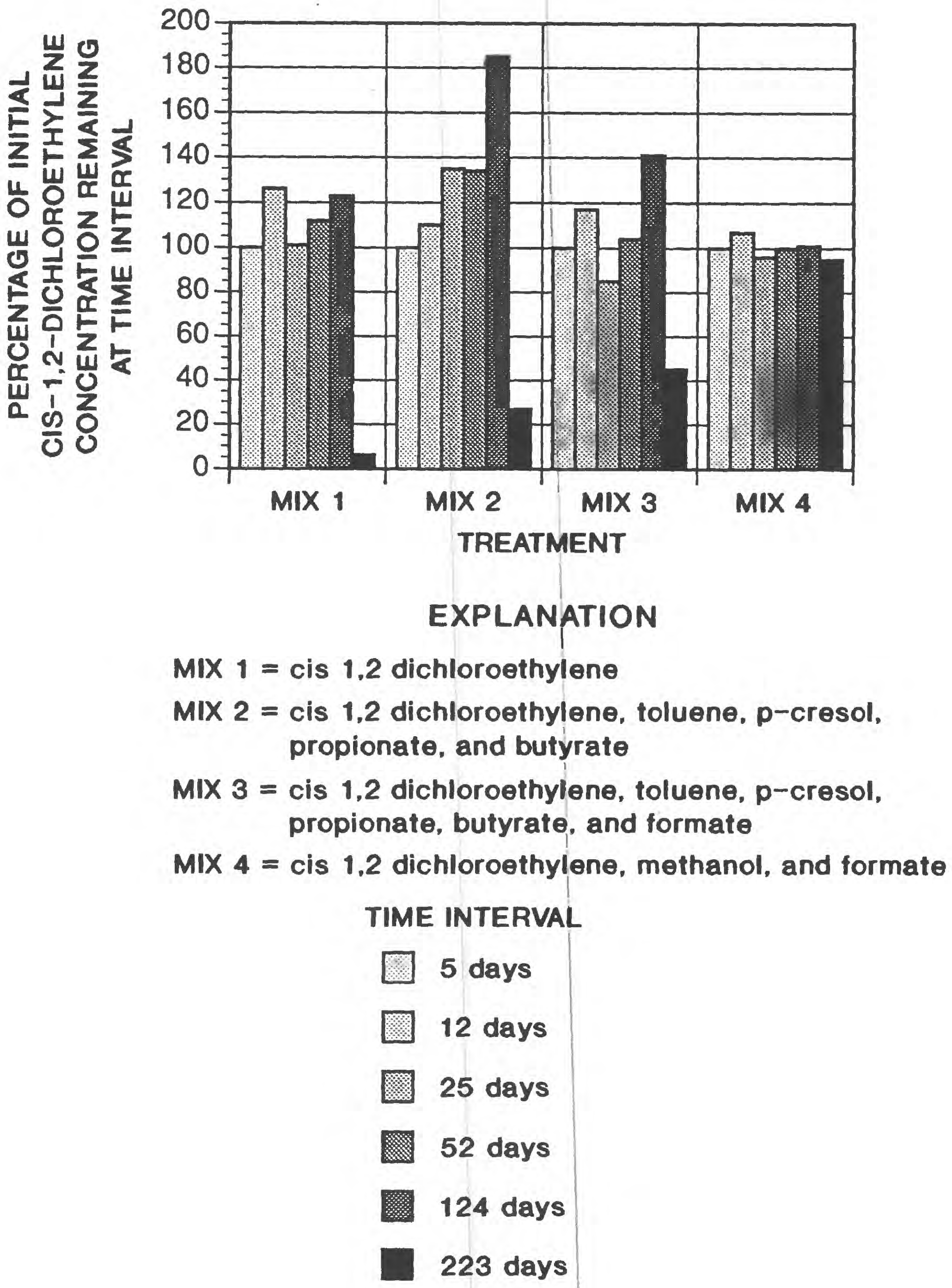


Figure 6. Effect of electron donor on biotransformation of cis-1,2-dichloroethylene in soil microcosms from site 4 at Picatinny Arsenal, New Jersey, at various time intervals.

methanol and formate can serve as effective electron donors to sustain reductive dechlorination of PCE and TCE (Freedman and Gossett, 1989). In microcosms that were amended with p-cresol and toluene, the concentration of toluene increased linearly up to 18 weeks. These results suggest that the increased toluene concentration might be the result of dehydroxylation of p-cresol, forming toluene. This explanation is contradicted by other studies, however (Häggblom and others, 1990). The concentration of toluene decreased nearly to undetectable levels between weeks 18 and 32, indicating almost complete biotransformation.

CONCLUSIONS

Slight to extensive biotransformation of cis-1,2-DCE (and apparently TCE) under methanogenic conditions occurred in microcosms constructed with soil from within the TCE plume at Picatinny Arsenal. Removal of cis-1,2-DCE appeared to occur after an adaptation period of about 18 weeks. After adaptation, nearly complete cis-1,2-DCE removal (94 percent) after 32 weeks occurred in microcosms constructed with soil from site 4. Smaller, but significant, removal of cis-1,2-DCE occurred in microcosms from other sites, where the maximum *in situ* concentration of cis-1,2-DCE ranged from 3.2 µmol (310 µg/L) to 2.3 µmol (220 µg/L). The first-order rate of cis-1,2-DCE biotransformation after adaptation (weeks 18 through 32) ranged from 0.01 per week to 0.18 per week within the TCE plume. Biotransformation of cis-1,2-DCE was most rapid at site 4, where *in situ* TCE and cis-1,2-DCE concentrations (at the depth of soil-core collection) were 2,000 and 58 µg/L, respectively. The aqueous concentrations of VC *in situ* were not in agreement with computed biotransformation rates, suggesting that high *in situ* VC concentrations may reflect active biotransformation processes upgradient, and subsequent transport of VC to other locations within the plume.

Only slight removal of cis-1,2-DCE (0.005 per week) occurred in soil microcosms constructed from soil cores collected from outside the contaminated area (site 6).

Amendment of soil microcosms from site 4 with a series of cocontaminants (electron donors) inhibited biotransformation of cis-1,2-DCE under methanogenic conditions. Amendment with a combination of methanol and formate resulted in nearly complete inhibition of cis-1,2-DCE degradation, whereas amendment with toluene, p-cresol, propionate, butyrate, and formate (in combination) resulted in the least inhibition.

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SIMULATION OF REACTIVE MULTISPECIES TRANSPORT IN TWO-DIMENSIONAL GROUND-WATER-FLOW SYSTEMS

By Mary Martin[1]

ABSTRACT

A model code, developed by modifying an existing two-dimensional nonreacting solute-transport model to simulate the transport of an unlimited number of species subject to user-defined chemical reactions and sorptive processes, is described. Simulation results that duplicate previously published results, and simulations of simultaneous solute and energy transport and of hydrocarbon transport and degradation, show that the code accurately simulates multispecies movement and interaction and is a useful tool for the analysis of contaminant fate and transport.

INTRODUCTION

The fate and transport of trichloroethylene (TCE) in ground water at Picatinny Arsenal, N.J., is being investigated by using solute-transport simulation techniques. The analysis of field-scale chemical, sorptive, and microbial processes that influence TCE transport requires simultaneous simulation of thermal energy and several solutes (multispecies transport) in a complex, multidimensional flow system. Traditional approaches to the simulation of ground-water contamination involve the description of (1) the transport of a single, nonreactive solute; (2) the simultaneous transport of several solutes, accomplished by incorporating equilibrium reaction approximations into a single transport equation; or (3) the transport of several solutes, accomplished by first solving for physical transport alone, then simulating the chemical interactions, and iterating between the solutions until a satisfactory level of convergence is reached. The disadvantages of these approaches include difficulty in obtaining iterative solutions, excessive computer time and storage requirements, and oversimplification of the physical or chemical processes.

This paper describes a model code, developed by modifying an existing nonreacting transport model, to simulate the transport of an unlimited number of species subject to user-defined chemical reactions and sorptive processes. The paper also illustrates the verification and application of this model by reproducing previously published results obtained by using other model codes, and by presenting hypothetical examples of simultaneous energy and solute transport and of one-dimensional hydrocarbon transport with idealized reactions representing biodegradation.

CODE MODIFICATIONS

The model code presented here is a modification of the U.S. Geological Survey solute-transport code SUTRA (Voss, 1984). The modified SUTRA code described herein is called MST and is referred to as "the model" or "the MST code" in this paper. The SUTRA code employs a two-dimensional hybrid finite-element and integrated-finite-difference method to simulate density-dependent saturated or unsaturated ground-water flow and the transport of thermal energy or a single solute subject to equilibrium sorption and production or decay. Table 1 summarizes the simulation capabilities of the SUTRA and MST codes. The MST code implements the same form of the partial differential equations for the fluid, energy, and solute mass balances as those used in the SUTRA code (Voss, 1984, p. 34, 38, and 42). The MST code retains all the simulation capabilities of the SUTRA code and simulates flow and transport from input data sets compiled for the SUTRA model. The MST code also simulates the transport and reaction of any number of species. These species can be all solutes or can be solutes and thermal energy. The mathematics that describe the chemical reactions must be programmed by the user. The reaction calculations are solved after the flow and transport calculations have been completed for each time step. The MST code is highly flexible and generalized and is suited for simulating a wide range of transport and chemical processes under various field conditions.

Table 1. *Summary of simulation capabilities of the SUTRA and MST solute-transport codes*

SUTRA Code	MST Code
Two-dimensional	Same
Hybrid Galerkin-finite-element method and integrated finite-difference method	Same
Quadrilateral finite-elements	Same
Bilinear basis functions	Same
Backward finite-difference in time	Same
Steady-state or transient flow and transport	Same
Saturated and(or) unsaturated flow	Same
Isotropic or anisotropic flow and transport parameters	Same
Single-species or energy transport	Multispecies and(or) energy transport
Areally constant adsorption parameters	Areally variable adsorption parameters
Areally constant production/decay parameters	Areally variable production/decay parameters
Single-species (solute or energy) density-dependent flow	Same
Single-species reaction chemistry (using adsorption and production/decay parameters)	User-supplied multispecies reaction
Single-fluid source or sink per node	Multiple-fluid sources or sinks per node

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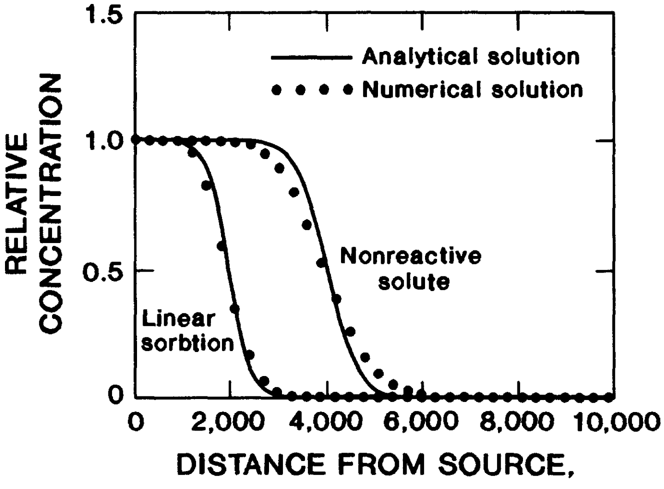
The methodology used to modify SUTRA is similar to that presented by Lewis and others (1987). Their approach simulates specific types of chemical reactions that were formulated such that their solution was compatible with the solution algorithms used in an existing transport code similar to SUTRA. Their approach requires the chemical reactions to be formulated such that the nonlinear terms can be incorporated into coefficients in the transport equation of the solute that sorbs. At each time step following the solution of the transport equations, a system of algebraic expressions that define the chemical interactions is solved simultaneously to obtain solute concentrations. All chemical-equilibrium calculations are solved separately from the advective-dispersive flow calculation, including the calculation of the nonlinear terms.

The major modifications to the SUTRA code include (1) changing the input and output subroutines to handle any number of species, (2) increasing the dimensions of the arrays pertaining to the concentration and chemical attributes of the transported solute, (3) repeating the solute-transport calculations for each species, and (4) adding the appropriate subroutine calls and variable transfers to a reaction subroutine at the end of each time step. The variables representing the sorption coefficients and the production/decay rates were changed to arrays that could represent areally distributed values at each node for each species.

EXAMPLE SIMULATIONS

Results simulated by using the MST code were compared to analytical solutions (Van Genuchten and Alves, 1982) for one-dimensional transport with linear sorption and nonreactive transport (fig. 1). This simulation serves to verify the accuracy of the results when simulating the transport of two solutes simultaneously. Results simulated by using the MST code also were compared to simulation results from Lewis and others (1987) of transport with linear sorption and a single aqueous complexation reaction involving the sorbing species (fig. 2). The basic set of transport equations solved by the MST code for this simulation are the same as those presented by Lewis and others (1987, p. 87 and 89). This simulation demonstrates the capability of the MST code to simulate the transport of two reacting solutes. Most other simulation results presented by Lewis and others (1987) were reproduced by using the MST code, but are not shown. These simulations included additional model capabilities, such as two-dimensional flow, transport of three solutes, and complexation of two solutes with one sorbing solute. The reaction subroutine used for these simulations was the same as that used by Lewis and others (1987). Results simulated by using the MST code agree closely with the analytical solutions and with previously published simulation results.

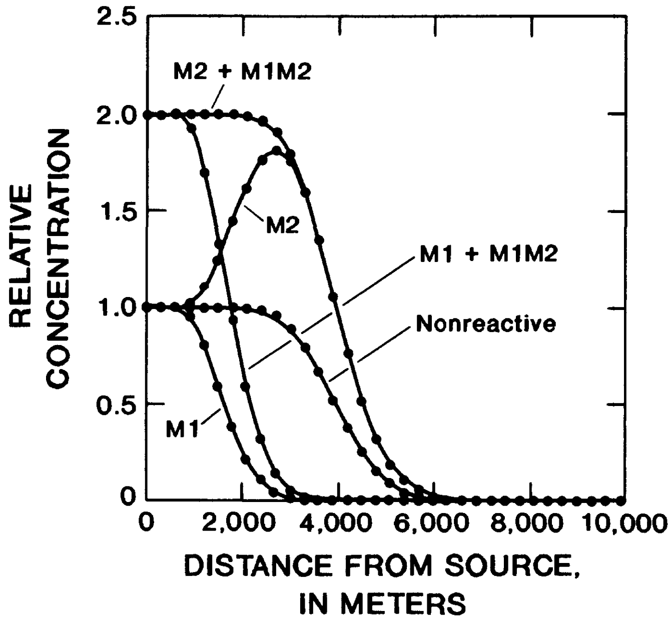
A simulation of simultaneous solute and energy transport in a flow field in a 150-m (meter) by 150-m vertical section of an aquifer was made. Temperature differences between the top and bottom boundaries cause the flow field to develop, with dense water at a constant temperature of 20 °C (degrees Celsius) at the top and lighter water at a temperature of 60 °C at the bottom. Buoyancy causes the lighter water to rise and form two convection-flow cells,



Simulation data

Length of simulation, 12,000 days
Time-step interval, 300 days
Number of quadrilateral elements, 100
Size of elements, 100 meters x 100 meters
Porosity, 0.2
Solid grain density, 2,650 kilograms/meter^3
Longitudinal dispersivity, 33 meters
Transverse dispersivity, 0 meters
Constant-head conditions
  Left side, 85 meters
  Right side, 0 meters
Initial solute concentrations (relative to nonreactive-solute source concentration)
  Nonreactive and sorbing solutes, 0.0 everywhere
Relative source concentrations
  Nonreactive and sorbing solutes, 1.0 at 0 meters
Fluid velocity, 0.3339 meters/day
Relative source concentrations, 1.0 at 0 meters
Linear sorption coefficient,
  0.1 kilogram of solute per kilogram of solid matrix

Figure 1. Single-species sorption and nonreactive transport.



EXPLANATION

● ● ● ● Simulated by using MST code

——— Simulated by Lewis and others (1987, fig. 7)

Simulation data

Same as figure 1, except:
Solutes, M1, M2, M1M2, and nonreactive solute
Source concentrations (relative to nonreactive-solute source concentration)
  Total dissolved M1 + M1M2, 2.0 at 0 meters
  Total dissolved M2 + M1M2, 2.0 at 0 meters
  Nonreactive solute, 1.0 at 0 meters
Linear sorption coefficient for M1, 0.25 kilogram of solute per kilogram of solid matrix
Aqueous complexation reaction, M1 + M2 = M1M2
Equilibrium constant, 1.0

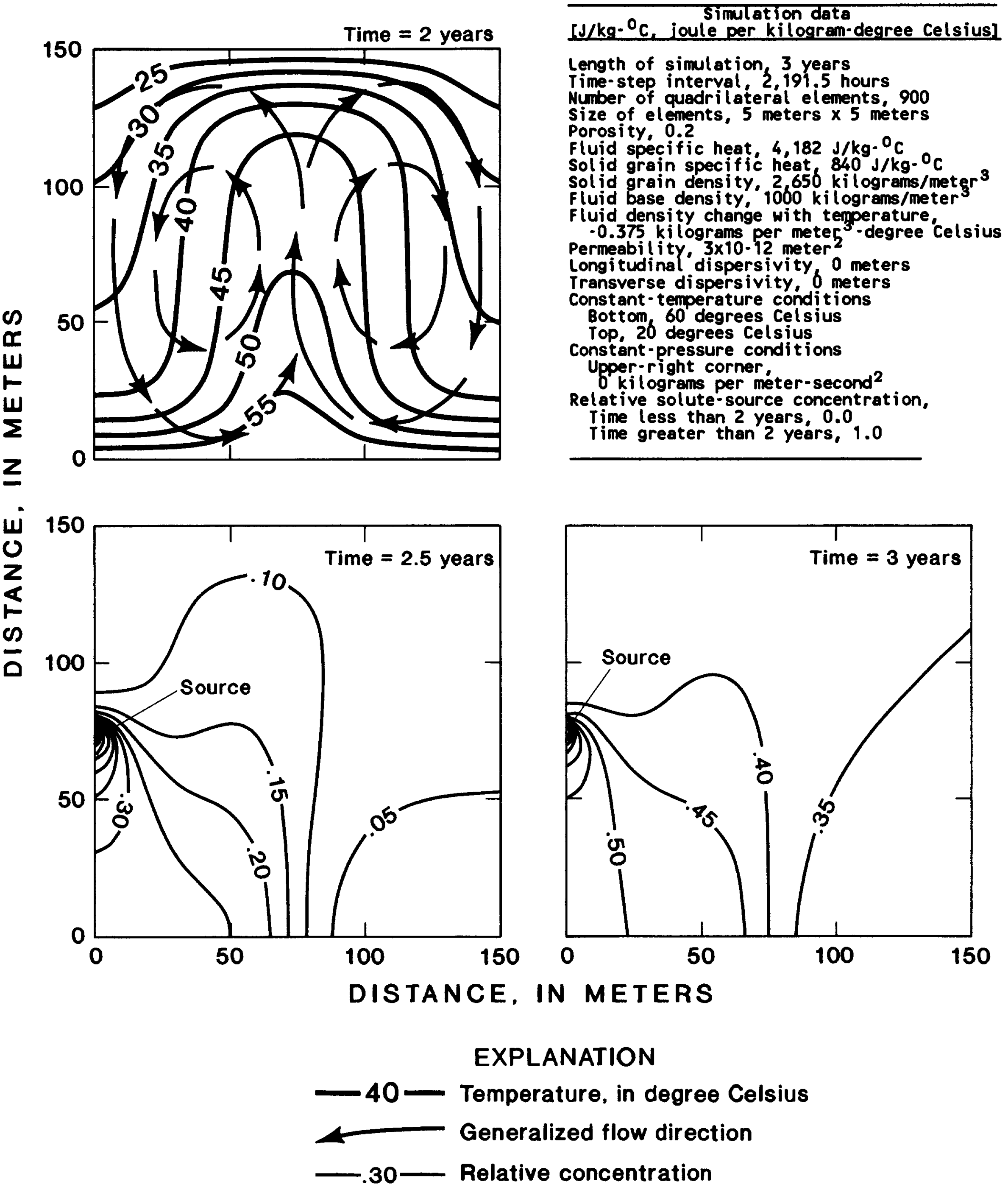
Figure 2. Simulated transport with equilibrium sorption of M1, aqueous complexation between M1 and M2, and a nonreactive solute.

with upward flow between them, in the center of the flow field (fig. 3). This flow pattern is similar to the free-convection flow cells discussed by Donaldson (1962, p. 3454 and fig. 2). The flow pattern is nearly stable after 2 years of simulation, but becomes unstable for simulations longer than those discussed here. The design and data for this simulation were compiled and tested by C.I. Voss (U.S. Geological Survey, written commun., 1990). Figure 3 shows the movement of a conservative solute away from a constant concentration source at the center of the left side of the flow field, and the data used in this simulation. This simulation demonstrates the model's capability to simulate simultaneous transport of solutes and energy. Such simulations are particularly applicable to studies of nuclear-waste disposal.

Simulation results of hydrocarbon transport influenced by idealized reactions representing biodegradation are shown in figure 4. Hydrologic data and approximations of chemical interactions used in this example are listed in figure 4. This simulation shows the capability of the MST code to simulate transport of interacting solutes and a subsequent product. The model simulates a one-dimensional flow field with instantaneous interaction between overlapping plumes of oxygen, a hydrocarbon, and a degradation inhibitor. For the purposes of this example, a hypothetical hydrocarbon is assumed to undergo aerobic degradation in the presence of oxygen, except where the inhibitor is present at a specified concentration. The upper graph shows the species concentrations (relative to the hydrocarbon source concentrations of 1.0) after 6,000 days of hypothetical nonreactive transport. Initial concentrations were zero for all species except the hydrocarbon, which had an initial concentration of 1.0 everywhere. Solute sources are at 0 and 5,000 m for oxygen, at 0 m for the hydrocarbon, and at 6,000 m for the inhibitor.

The approximations for degradation have been highly simplified for the purposes of exhibiting the capabilities of the MST code and were based on the assumption of instantaneous reactions. The simulated species distributions in the lower graph in figure 4 exhibit (1) aerobic degradation of the hydrocarbon in the presence of oxygen, (2) the supression of aerobic degradation in the presence of an inhibitor, and (3) the formation and transport of a degradation product. Borden and Bedient (1986) show that simulated hydrocarbon distributions in ground water have a weak sensitivity to microbial kinetics, and conclude that aerobic biodegradation can be approximated as an instantaneous reaction between oxygen and hydrocarbon for field conditions. The explicit, finite-difference form of their approximation is used to simulate aerobic degradation and is shown in figure 4 (eq. 1 and 2). In this example, oxygen is the electron acceptor and the ratio of oxygen to hydrocarbon consumed is 2. A hypothetical inhibitor was hypothesized for this simulation, and no aerobic degadation was allowed when the inhibitor concentrations were greater than 0.25 relative to the hydrocarbon source concentration of 1.0. Comparison of the species distributions under reacting and nonreacting conditions shows zones of depleted concentrations of oxygen and hydrocarbon caused by the degradation approximations (fig. 4). The length of each zone differs near the two oxygen plumes because of the presence of the inhibitor at a distance of 6,000 m.

Other model capabilities that have not been illustrated in this paper include the representation of areally variable distributions of the sorption coefficients and the rates of mass production in the input data. These data are varied by



Simulation data
[J/kg-°C, joule per kilogram-degree Celsius]

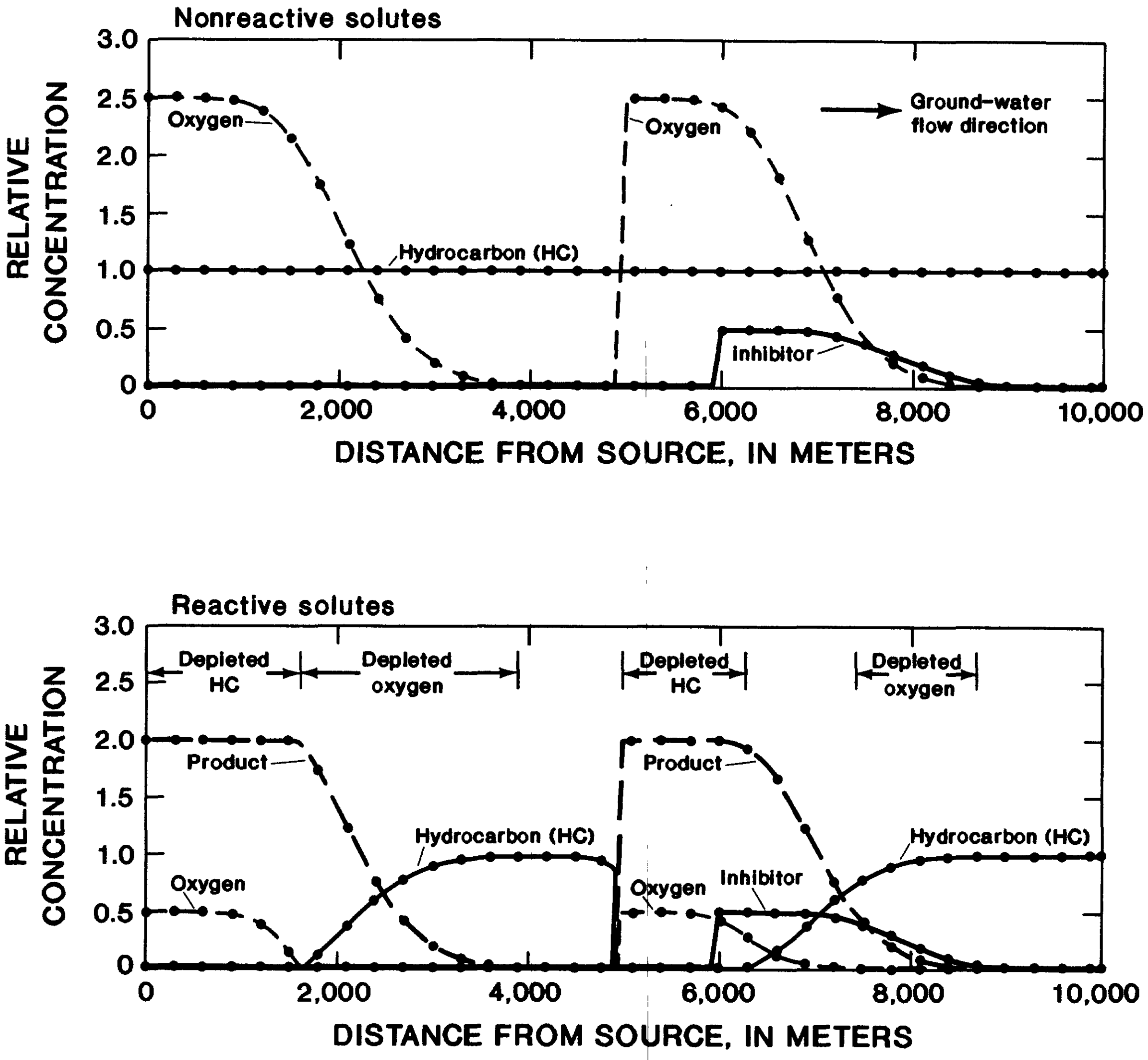
Length of simulation, 3 years
Time-step interval, 2,191.5 hours
Number of quadrilateral elements, 900
Size of elements, 5 meters x 5 meters
Porosity, 0.2
Fluid specific heat, 4,182 J/kg-°C
Solid grain specific heat, 840 J/kg-°C
Solid grain density, 2,650 kilograms/meter^3
Fluid base density, 1000 kilograms/meter^3
Fluid density change with temperature,
  -0.375 kilograms per meter^3-degree Celsius
Permeability, 3x10-12 meter^2
Longitudinal dispersivity, 0 meters
Transverse dispersivity, 0 meters
Constant-temperature conditions
  Bottom, 60 degrees Celsius
  Top, 20 degrees Celsius
Constant-pressure conditions
  Upper-right corner,
   0 kilograms per meter-second^2
Relative solute-source concentration,
  Time less than 2 years, 0.0
  Time greater than 2 years, 1.0

Figure 3. Simulated temperature distribution, generalized flow directions, and concentration distribution for simultaneous energy and solute transport.

identifying a scaling factor for each model node and multiplying the sorption coefficients and production rates for each species by this factor. Another model capability allows multiple fluid sources at each node, which simplifies the preprocessing of multiple-solute concentrations in multiple-fluid sources.

ONGOING WORK

The simulation results presented here demonstrate that the MST code is an accurate and useful tool for the simulation of multispecies movement and interaction in the analysis of contaminant fate and transport. Other



Simulation data

Length of simulation, 6,000 days
Time-step interval, 300 days
Number of quadrilateral elements, 100
Size of elements, 100 meters x 100 meters
Porosity, 0.2
Solid grain density, 2,650 kilograms/meter^3
Longitudinal dispersivity, 33 meters
Transverse dispersivity, 0 meters
Fluid velocity, 0.3339 meters/day
Constant-head conditions
  Left side, 85 meters
  Right side, 0 meters
Initial solute concentration (relative to HC)
  HC, 1.0 everywhere
  Oxygen and inhibitor, 0.0 everywhere
Relative solute-source concentration
  HC, 1.0 at 0 meters
  Oxygen, 2.5 at 0 and 5,000 meters
  Inhibitor, 0.5 at 6,000 meters

Chemical approximations

$HC(t+1) = HC(t) - O(t)/2,$ (1)
$O(t+1) = 0.0,$ and
$P(t+1) = O(t)$
where $I(t) < 0.25$ and $HC(t) > O(t)/2$

$HC(t+1) = 0.0,$ (2)
$O(t+1) = O(t) - HC(t) \times 2,$ and
$P(t+1) = 2 \times HC(t)$
where $I(t) < 0.25$ and $HC(t) < O(t)/2$

and where:
HC is concentration of hydrocarbon
O is concentration of oxygen
P is concentration of product
I is concentration of inhibitor
t is time at end of current time step
t+1 is time at beginning of next time step
< is less than
> is greater than

Figure 4. Simulated hydrocarbon transport and degradation.

simulations are planned to test further the capabilities of the MST code, including the ability to simulate areally distributed sorption and production coefficients.

The MST code is being used to simulate the fate and transport of TCE in ground water in a stratified glacial-valley aquifer at Picatinny Arsenal. A two-dimensional cross-sectional model along the axis of a contaminant plume in an unconfined aquifer is being developed to analyze the effects of advection, dispersion, sorption, microbial degradation, and volatilization of TCE under field conditions. Field data on the site hydrogeology and water quality have been compiled and analyzed; these data are being used in the design of the transport model and in the analysis of simulation results. In addition, a three-dimensional ground-water flow model of the area has been calibrated (Voronin, 1991, this Proceedings).

Although highly simplified, the interactions used in the previously presented examples can be expanded to describe the degradation of TCE in ground water at Picatinny Arsenal. Although TCE is resistant to degradation under aerobic conditions, aerobic cometabalism of TCE in the presence of methane is described by Lanzarone and McCarty (1990) and may be important at the contaminant site (Ehlke, 1988). Additional approximations can be programmed to simulate anaerobic degradation of TCE in the presence of an electron donor. The most likely sources of this donor are reduced hydrocarbon compounds other than TCE, such as methane. Certain trace elements, sulfate, oxygen, and pH are possible inhibitors of the anaerobic degradation of TCE (T.A. Ehlke, U.S. Geological Survey, oral commun., 1990) in a manner similar to that shown in the last example simulation. Although the assumption of instantaneous reactions probably is not applicable to degradation of TCE under field conditions, functions describing degradation kinetics (Monad or Michaelis-Menten functions) can be programmed into the subroutine describing chemical interactions. Preliminary simulations of single-species transport at the field site have been made, and reactions involving dissolved TCE and other solutes or energy are being attempted.

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REDUCTIVE DECHLORINATION OF TRICHLOROETHYLENE IN ANOXIC AQUIFER MATERIAL FROM PICATINNY ARSENAL, NEW JERSEY

By Barbara H. Wilson[1], Theodore A. Ehlke[2], Thomas E. Imbrigiotta[2], *and* John T. Wilson[3]

ABSTRACT

Ground water at Picatinny Arsenal, New Jersey, has been contaminated with chlorinated solvents released from the waste water-treatment system of a metal-plating shop and from overflow from a degreasing vat. Trichloroethylene is the major contaminant, but 1,1,1-trichloroethane and tetrachloroethylene are also present. Cis-1,2-dichloroethylene and vinyl chloride were not original contaminants, but their accumulation in the ground water indicates reductive dechlorination of the trichloroethylene and tetrachloroethylene released to the aquifer. Laboratory microcosms were used to estimate the kinetics of reductive dechlorination at field scale. The microcosms were constructed with aquifer material collected from locations along the longitudinal extent of the plume and from outside the area of contamination. To determine whether supplementary electron donors would enhance reductive dechlorination, three suites of electron donors were added to aquifer material: (1) butyrate, propionate, toluene, and p-cresol; (2) butyrate, propionate, formate, methanol, toluene, and p-cresol; or (3) formate and methanol.

Preliminary results indicate that sorption and biological processes are important removal mechanisms. First-order rate constants in the microcosm study ranged from 0.004 to 0.02 per week and compared favorably to estimated first-order rate constants from field values of 0.03 to 0.09 per week. Reductive dechlorination was not enhanced in microcosm experiments in which alternate electron donors were added.

INTRODUCTION

Chlorinated solvents are widely used for metal cleaning and degreasing. The most commonly used solvents are trichloroethylene (TCE), 1,1,1-trichloroethane (TCA), and tetrachloroethylene (PCE). Inappropriate disposal of the solvents contaminates the subsurface environment and eventually contaminates the ground water. These chlorinated solvents are not generally biologically transformed in oxygenated ground waters, but do undergo reductive dechlorination in anoxic environments. TCE is the daughter product of PCE by reductive dechlorination, and TCE may be further transformed into the dichloroethylenes and vinyl chloride (VC) (Vogel and McCarty, 1985; Barrio-Lage and others, 1986).

The ground water at Picatinny Arsenal was contaminated by disposal of metal-plating wastes in unlined lagoons and onto the ground. The major chlorinated contaminant is TCE, but PCE, TCA, cis-1,2-dichloroethylene (DCE), and VC are also found. Metals commonly used in plating solutions, such as chromium, cadmium, copper, lead, nickel, vanadium, and zinc, were also found in the ground water. Additional contaminants from the metal-plating operation were sodium, potassium, sulfate, chloride, and cyanide.

Two parallel laboratory studies were conducted to estimate the kinetics of TCE or cis-1,2-DCE dechlorination. Because reductive dechlorination depends on the availability of electron donors (Baek and Jaffé, 1989; Freedman and Gossett, 1989;), each study amended additional microcosms with a series of potential electron donors. This paper discusses the preliminary results of the TCE fate study. Results of the cis-1,2-DCE fate study are presented by Ehlke and others (1991, this Proceedings).

SITE DESCRIPTION

The contamination is located in an 11-m (meter) thick unconfined glacial-stratified-drift aquifer underlain by a confining unit composed of interbedded fine sand, silt, and clay. The water table ranges from 1.5 to 5 m below land surface. A confined stratified-drift aquifer, 7 to 25 m thick, lies below the confining unit. The contaminant plume extends approximately 500 m downgradient until the ground water discharges into Green Pond Brook (fig. 1).

In September 1989, aquifer material from five locations within the contaminant plume and three locations outside the plume was obtained for microcosm fate studies (fig. 1). Aseptic coring techniques developed by Leach and others (1988) were used to collect the samples. The aquifer material was stored in sterile canning jars and transported to the laboratory on ice.

Water samples from adjacent monitoring wells were collected at depths corresponding to the core material. The water was analyzed for concentrations of dissolved oxygen, methane, iron (Fe^{2+}), alkalinity, and total organic carbon; redox potential; pH; and bacteria counts (table 1). The water analyses are important to describe the geochemical nature of the subsurface at the time of core collection.

MICROCOSM CONSTRUCTION

The chemicals used were high-purity TCE, toluene, *p*-cresol, methanol, sodium butyrate, sodium formate, and sodium propionate. The purities of all chemicals were at least 97 percent.

Approximately 110 grams of aquifer material (wet weight) was transferred to sterile 60-mL (milliliter) serum bottles for construction of the microcosms. All manipulations were performed in an anaerobic glovebox to maintain the anoxic nature of the aquifer material. Dosing solutions of the volatile compounds were prepared by adding the pure chemicals to autoclaved water and stirring without headspace overnight.

One mL of the dosing solution(s) containing TCE or TCE and one of the electron-donor amendments was added to each microcosm; the bottles were then capped with a

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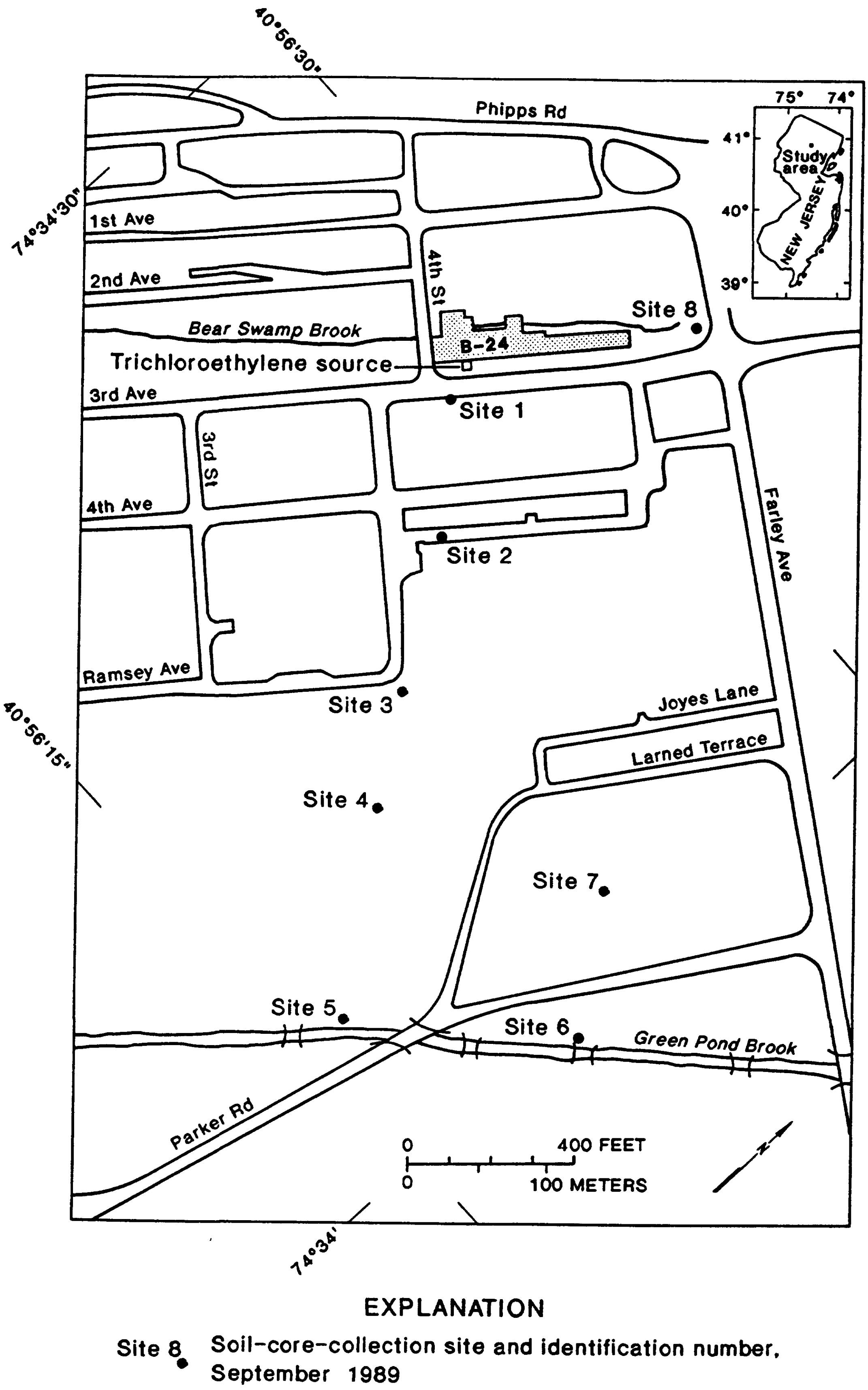
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Ramsey Ave
4th St
3rd St
B-24
Site 1
Site 2
Site 3
Site 4
Site 5
Site 6
Site 7
Site 8
Farley Ave
Joyes Lane
Larned Terrace
Green Pond Brook
Parker Rd
0
400 FEET
0
100 METERS
75°
74°
41°
40°
39°
Study area
NEW JERSEY
EXPLANATION
Site 8
Soil-core-collection site and identification number, September 1989

Figure 1. Location of cores taken for anaerobic microcosm studies. Sites 1 to 5 are in the contaminant plume. Site 1 is near the source area at Building 24. Sites 6 to 8 are outside the contaminant plume, and are uncontaminated with respect to TCE.

Table 1. *Geochemistry of water at Picatinny Arsenal, September 1989*

[Concentrations are presented for screened interval closest to depth soil cores collected, m = meters; mg/L = milligrams per liter; µg/L = micrograms per liter; mv = millivolts; TOC = total organic carbon; NA = not analyzed; < = less than; AODC = acridine orange direct counts; mL = milliliters]

Sample well	Sample depth (m)	Dissolved oxygen (mg/L)	Methane[1] (µg/L)	Redox (mv)	Iron, Fe^{2+} (mg/L)	pH	Alkalinity (mg/L)	TOC (mg/L)	AODC bacteria/ (mL)
From the contaminant plume									
Site 1	9.4	0.5	34	+101	0.1	6.6	100	5.5	2.2×10^3
Site 2	11.0	.5	48	-131	.4	6.5	92	2.9	1.5×10^4
Site 3[2]	7.0	6.0	9	NA	<.05	7.2	154	1.7	2.3×10^4
Site 4	6.4	1.6	4	+142	.2	5.7	34	.4	7.4×10^3
Site 5	11.0	7.2	110	+123	<.05	6.9	100	.1	1.1×10^4
From outside the contaminant plume									
Site 6	7.3	1.8	NA	+ 13	.3	6.9	116	.6	1.5×10^4
Site 7	11.3	.6	<1	+186	<.05	6.2	74	.3	NA
Site 8	7.0	.2	118	-127	10.4	6.1	84	5.5	NA

[1] Collected June 1989.

[2] Sample collected during heavy rain; water level was at top of well because of rain.

Teflon[4]-coated gray butyl rubber stopper and a crimp-cap seal. The electron donors were (1) 0.1 mM (millimolar) butyrate, propionate, toluene, and *p*-cresol; (2) 0.1 mM, respectively, of butyrate, propionate, toluene, and *p*-cresol, and 1.0 mM formate and methanol; or (3) 1.0 mM formate and methanol.

Sterile controls were autoclaved for 1 hour on 2 consecutive days at 121 °C (degrees Celsius) before the addition of the dosing solution. The microcosms were mixed and then stored inverted in an anaerobic incubator jar under a nitrogen atmosphere. The samples were stored in the dark at 18 °C.

SAMPLE ANALYSES

Three microcosms from each site were sacrificed for headspace analyses at each sampling interval. Each microcosm was well shaken, then heated at 70 °C for 30 minutes in a water bath before analysis. Propane was added to the headspace as an internal standard; the sample size was 200 microliter. The gas chromatographic column used was a DB 624, 30-m by 0.53-millimeter inside diameter. After injection, the column was held at 30 °C for 5 minutes; heat was then increased at a rate of 8 °C per minute to 175 °C and held at that temperature for 10 minutes. Detection was by flame ionization. Concentrations of dissolved oxygen, alkalinity, and Fe^{2+} and measurements of pH and redox potential were determined by standard U.S. Environmental Protection Agency methods (U.S. Environmental Protection Agency, 1979). Bacteria counts were determined by acridine orange direct counts (AODC) (Wilson and others, 1983). Headspace methane concentrations for the field water samples were determined by the method of Kampbell and others (1989).

RESULTS AND DISCUSSION

Preliminary results of the TCE-fate study are shown in table 2. Removal of TCE in excess of removal in the autoclaved controls was observed at sites 1 and 5 in the plume and site 6 outside the plume. The greatest removals were seen at sites 5 and 6, where concentrations of 32 percent and 28 percent of the initial concentration, respectively, remained at the end of 25 weeks (table 2). There was no obvious correlation between TCE dechlorination and the chemistry of the ground water (table 1). The biologically active material was collected from sites located adjacent to Green Pond Brook (fig. 1) where there is a shallow layer of peat. The cores were collected from beneath the narrow peat layer approximately 1 m below land surface. The peat did not appear to be incorporated into the samples used to construct microcosms. However, the amount of soil organic matter may be higher in that part of the aquifer and, thus, may be an electron donor to the dechlorination process. At the same time, the soil organic matter would efficiently sorb the TCE from the infiltrating ground water.

First-order rate constants were calculated for TCE transformation between weeks 4 and 25 (table 2). Sorption processes are assumed to be the dominant removal process between weeks 0 and 4. Based on these calculations, the

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[4] The use of brand, firm, or trade names in this paper is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

Table 2. *Distribution of trichloroethylene in aquifer material from Picatinny Arsenal*

[µg/L = micrograms per liter; TCE = trichloroethylene]

Sample location	TCE concentrations in micrograms per liter, after indicated number of weeks of incubation:			Percentage remaining	Rate of depletion (per week)
	0	4	25		
Contaminant plume					
Site 1	340	320	210	62	0.02
Site 2	430	320	320	74	.00
Site 3	360	360	280	78	.012
Site 4	980	930	790	81	.008
Site 5	380	130	120	32	.004
Outside the contaminant plume					
Site 6	145	100	40	28	.04
Autoclaved control					
Site 8	200	200	180	90	.005
Electron donor					
Site 4					
Group I[1]	240	240	250	104	-.002
Group II[2]	1,280	800	700	55	.006
Group III[3]	940	850	730	78	.007

[1] Butyrate, propionate, toluene, and *p*-cresol.

[2] Butyrate, propionate, formate, methanol, toluene, and *p*-cresol.

[3] Formate and methanol.

fastest biological removals appear to be in sites 1 and 3 (0.02 and 0.012 per week, respectively) within the plume and site 6 (0.04 per week) outside the plume. The remaining rate constants, including those from the electron donor treatments, appear to be equivalent to the constant calculated for the autoclaved controls (-0.002 to 0.008 per week).

The laboratory rate constants are consistent with the behavior of the plume at field scale. The highest concentration of TCE in the plume in late 1989 was 25,000 µg/L (micrograms per liter) at site 3. The highest concentration at site 5, 220 m downgradient, was 1,400 µg/L. At an average seepage velocity of 0.3 to 0.9 meters per day, this corresponds to a field first-order rate constant for TCE depletion between site 3 and site 5 of 0.08 to 0.03 per week. The highest concentration at site 4, which is 140 m upgradient from site 5, is 10,000 µg/L. This corresponds to a field first-order rate constant for TCE depletion between site 4 and site 5 of 0.09 to 0.03 per week. Further analysis of field and laboratory rate constants is in progress.

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COMPARISON OF FOUR METHODS FOR SAMPLING AND ANALYZING UNSATURATED-ZONE WATER FOR TRICHLOROETHENE AT PICATINNY ARSENAL, NEW JERSEY

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ABSTRACT

Four methods of collecting samples of unsaturated-zone water for quantitative analysis for trichloroethene were compared at Picatinny Arsenal in Morris County, New Jersey. For all four methods, water is transferred from a depth of 2 meters to land surface with a 0.15-meter-long suction lysimeter attached to a 1.85-meter length of 0.32-centimeter-outer-diameter stainless-steel tubing. For the first method (standard), water flows from the lysimeter into a 5-milliliter glass serum vial with a Teflon[3]-lined septum cap. Sample is withdrawn from the vial through a second line leading to a water trap and vacuum source. after 15 to 20 milliliters of water passes through the serum vial, the vial is disconnected and returned to the laboratory for analysis. For the second method (modified Bengt-Arne Torstensson), a vacuum line is connected to a 5-milliliter serum vial with a Teflon-lined septum cap. After causing a negative pressure of approximately 95 centibars, the vacuum is disconnected from the vial and the vial is connected directly to the stainless-steel tubing leading to the lysimeter. The negative pressure in the vial induces flow from the lysimeter to the vial. The water sample in the vial is transported to the laboratory for analysis after flow stops. For the third method (syringe), water flow is induced by vacuum from the lysimeter through a port connector attached to silicone tubing. The needle of a 5-milliliter gas-tight syringe is inserted through the silicone tubing so that the tip of the needle extends into the port connector. As water passes the tip of the syringe needle, the plunger of the syringe is extended to draw a sample into the barrel of the syringe. After sample collection, a Mininert valve at the end of the syringe is closed and the sample is transported to the laboratory in the syringe for analysis. For the final method (purge-and-trap), water flow is induced into a purge vessel by vacuum. An adsorbent trap is placed between the effluent end of the purge vessel and the vacuum source to capture trichloroethene that volatilizes from the water sample. Trichloroethene remaining in the water sample is purged onto the trap with helium and the trap is transported to the laboratory for analysis. All samples are analyzed for trichloroethene by gas chromatography. Statistical analysis of the data indicates that either the purge and trap or syringe methods can more accurately collect water samples from the vadose zone for quantitative analysis for trichloroethene relative to the modified Bengt-Arne Torstensson or standard methods.

INTRODUCTION

As part of a larger, ongoing study of the dynamics of trichloroethene (TCE) in the unsaturated zone above a contaminated water-table aquifer at Picatinny Arsenal in Morris County, N.J., the sampling and analysis of unsaturated-zone water for TCE is required. In this paper, four sampling methodologies for unsaturated-zone water are compared to determine the most suitable method for the accurate quantification of the concentration of TCE.

Picatinny Arsenal is located in north-central New Jersey (fig. 1). Beginning in 1960, Building 24 at Picatinny Arsenal was used for anodizing metals with chromic and sulfuric acids; cleaning, degreasing, and deburring metals; and plating metals with chromium, cadmium, copper, tin, and nickel (Benioff and others, 1990). The primary solvent used for metal degreasing was TCE. From 1960-81, wastewater from the degreasing operations was discharged into two unlined lagoons and to an unlined overflow dry well adjacent to Building 24 that had a combined volume of about 55,000 gallons (Benioff and others, 1990; Smith and others, 1990). As a result, the unconfined sand-and-gravel aquifer that underlies the site has been contaminated with TCE. The measurable ground-water contamination extends from Building 24 to Green Pond Brook and is shown by the vertically averaged isoconcentration lines in fig. 1. Additional details of the site's ground-water and unsaturated-zone contamination, lithology, hydrology, and source contamination history are given elsewhere (Imbrigiotta and Martin, 1988; Imbrigiotta and others, 1988; Martin, 1988; Smith and others, 1990). A site near the center of the TCE ground-water plume was selected for the field comparison of sampling methods (fig. 1).

MATERIALS AND METHODS

Twenty-five ceramic-cup suction lysimeters were installed at a depth of 2 m (meters) below land surface in a square grid pattern near the center of the TCE ground-water plume (fig. 1). The lysimeters were installed on June 11, 12, and 13, 1990. The grid consists of five rows and five columns, each separated by a 1-m distance. One lysimeter is located at each node point of the grid, and each lysimeter is numbered by its location in the grid according to matrix notation. For example, lysimeter 3-2 is located in row 3, column 2, of the grid. A subset of 14 lysimeters from this group consistently yielded water in sufficient quantities to allow consecutive sampling by four methods, and these lysimeters were subsequently used for this study.

The ceramic cup of each lysimeter has a length of 15 cm (centimeters), an outer diameter of 2.2 cm, and an inner diameter of 1.7 cm. The air-entry pressure of the lysimeter is 100 cbar (centibars). Prior to installation, solid glass bars (1.3-cm diameter) were inserted into the ceramic cups to minimize the volume accessible to inflowing water. The resulting volume of water required to saturate eac lysimeter is 6±1 mL (milliliters). Each lysimeter was the

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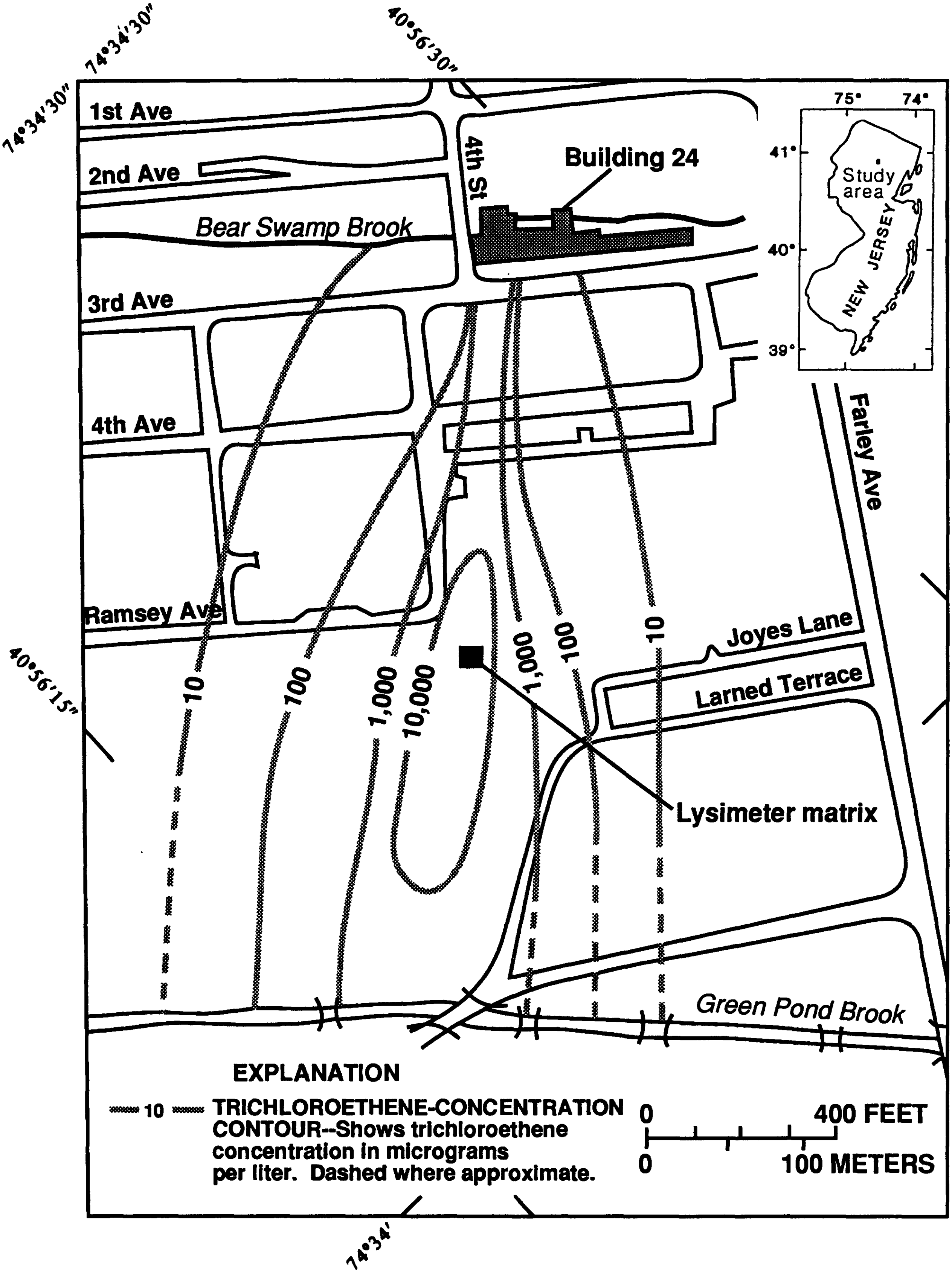
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Farley Ave
Joyes Lane
Larned Terrace
Lysimeter matrix
Green Pond Brook
10
100
1,000
10,000
1,000
100
10
40°56'15"
75°
74°
41°
40°
39°
Study area
NEW JERSEY
EXPLANATION
10 TRICHLOROETHENE-CONCENTRATION CONTOUR--Shows trichloroethene concentration in micrograms per liter. Dashed where approximate.
0
400 FEET
0
100 METERS
74°34'

Figure 1. Study area, showing locations of lysimeters and depth-averaged concentration lines of trichloroethene in ground water.

attached to a 1.85-m-long, 0.32-cm-outer-diameter by 0.21-cm-inner-diameter stainless-steel tube by a Swagelok connector fastened to a butyrate (plastic) cap on the ceramic cup. At land surface, the stainless-steel tubing was sealed with a Swagelok cap until ready for sampling.

Each lysimeter was installed by manually augering a 7.5-cm-diameter borehole with a bucket auger. After lowering the lysimeter into the borehole, a uniform sand (95 percent finer than 0.59-millimeter particle diameter) was poured down the hole and around the lysimeter to ensure that large void spaces were not in contact with the porous cup. Native soil was then used to fill the remainder of the borehole. Within 0.3 m of land surface, a 5-cm layer of bentonite was added to minimize any preferential transport of water or TCE along the disturbed borehole.

Figure 2 schematically shows the configuration of the equipment used to sample the lysimeters by each of four methods. Prior to collecting the first sample, 30± 5 mL of water were removed from the subsurface by vacuum along path 1-2-4-9 (fig. 2). This volume is approximately four to seven times the volume of water in the saturated lysimeter. The vacuum pressure applied to induce water flow was 80±15 cbar. Duplicate water samples were collected consecutively by each of the four methods. The sequential order of the four methods used to sample water was adjusted for each lysimeter so that each method was implemented in each of the four consecutive sampling positions about 25 percent of the time over the course of the study. For example, the Syringe (SYR) method was the first method used to sample approximately 25 percent of the lysimeters. Aside from the lysimeter, the only materials that contacted the collected samples were glass, stainless steel, or Teflon.

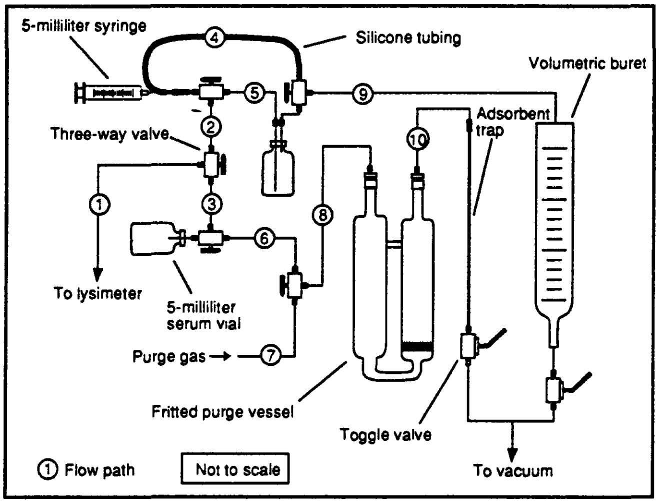

Figure 2. Schematic diagram of the configuration of sampling equipment used to sample unsaturated-zone water for trichloroethene by four methods. The flow paths (circled numbers) utilized in each method are described in text.

The first method chosen for study is called the Standard (STD) method and is implemented routinely to sample unsaturated-zone water for analysis of inorganic constituents (Wagner, 1962; Suarez, 1986). Flow of water is induced by vacuum through a 5-mL serum vial with a Teflon-lined silicone septum along path 1-2-5-9 (fig. 2). After approximately 20 mL of water exits the vial, the vial is disconnected and placed in an ice chest for transport to the laboratory for analysis of the sample.

The second method chosen for study is similar to the BAT (Bengt-Arne Torstensson) method described by Torstensson (1984) and is called the Modified BAT (MBAT) method. A vacuum pressure of 95 cbar is applied to a 5-mL serum vial by a syringe needle through the septum cap. After the vacuum is applied, the vial is disconnected from the vacuum source and is connected to the lysimeter so that flow is induced by the negative pressure present in the vial. Water then flows along path 1-3 (fig. 2). When the negative pressure in the vial equals the negative pressure in the lysimeter, flow of water to the vial stops, and the vial is transported to the laboratory in an ice chest for analysis of the sample.

The third method chosen for study is similar to a method used for sampling unsaturated-zone soil gas (Kerfoot, 1987) and is called the SYR method. As the flow of water is induced along path 1-2-4-9 (fig. 2) by vacuum, the needle of a 5-mL, gas-tight syringe is inserted through the silicone tubing so that the tip of the needle passes into a stainless-steel port connector. As water flows past the tip of the syringe needle, the plunger of the syringe is extended, causing water to flow into the syringe barrel. The withdrawal of the plunger is such that the rate of water inflow into the syringe is less than the rate of water flow from the lysimeter. In this manner, water that is sampled by the syringe is not exposed to the silicone tubing. After approximately 5.5 mL of water have entered the syringe barrel, a Mininert valve between the syringe needle and the syringe barrel is closed. The syringe assembly is then withdrawn from the silicone tubing, and the valve is opened momentarily to remove any air bubbles present in the syringe barrel (typically less than 0.3 mL). The valve is reclosed and the syringe is transported in an ice chest to the laboratory for analysis of the sample.

The fourth method chosen for comparison is similar to the method described by Wood and others (1981) and is called the purge-and-trap (P&T) method. Flow of water is induced by vacuum along path 1-3-6-8 (fig. 2) and into a 20-mL (nominal volume) purge vessel with a glass frit. The effluent end of the purge vessel is connected to a 30.5-cm-long stainless-steel adsorbent trap containing 7.6 cm of Carbopak B and 1.3 cm of Carbosieve S-III. The outer and inner diameters of the trap are 0.32 cm and 0.27 cm, respectively. (Prior to use in the field, all traps were conditioned at 260 °C (degrees Celsius) for 45 minutes on a Tekmar LSC 2000 purge-and-trap concentrator.) As the water sample is collected in the purge vessel, any TCE that volatilizes from the sample is retained by the trap. After 10 to 20 mL of sample is collected in the purge vessel, the influent line to the purge vessel is disconnected from the lysimeter and connected to a pressurized (15 pounds per square inch) source of helium with a three-way valve. At the same time, the effluent end of the trap is disconnected from the vacuum source and opened to the atmosphere. The helium purges TCE from the water sample for 11 minutes onto the adsorbent trap. The trap is disconnected from the purge vessel, sealed with Swagelok caps, and transported to the laboratory in an ice chest for later analysis. The volume of water in the purge vessel is measured with a graduated cylinder.

In the laboratory, the concentration of TCE in all water samples was measured quantitatively with a Tracor 540 gas chromatograph with a Volcol capillary column and a Hall electrolytic conductivity detector. Five-mL aliquots were purged for 11 minutes with a Tekmar LSC 2000 purge-and-trap concentrator. TCE was trapped with the Carbosieve/carbopack trap described previously and was desorbed at 230 °C for 3 minutes. For each analysis, the gas chromatograph was cooled initially to 30 °C with carbon dioxide and then was heated at a rate of 4 °C per minute from 30 °C to 140 °C, and 20 °C per minute from 140 °C to 230 °C. The final temperature was held constant for 3 minutes. The electrolytic solution for the detector was 100 percent n-propanol. The response of the detector was measured with a Nelson Analytical data system and was analyzed with Nelson's Turbochrom II software. The concentration of TCE was related to the response of the detector by analysis of a standard curve. Standards were prepared with a commercially certified TCE stock solution in methanol.

Samples collected on the adsorbent trap were analyzed by installing the trap in the LSC 2000 purge-and-trap concentrator and desorbing the sample into the gas chromatograph. The operating conditions of the gas chromatograph were identical to those described above.

Several precautions were taken to ensure the quality of the data. In addition to the generation of a standard curve prior to sample analysis, an additional standard and a water blank were analyzed with each group of eight field samples. Immediately prior to analysis, an internal standard (1-chloro-3-fluorobenzene) was added to each water sample collected in the field. (No internal standard was added to samples collected on the adsorbent traps.) Finally, a blank sample was transported to and from the field site for each method and for each sampling trip to determine whether samples were contaminated during the sampling trip. These "trip blanks" were analyzed for TCE in the laboratory in a manner identical to the analysis of actual samples. All water samples were analyzed within 36 hours of collection; all traps were analyzed within 72 hours of collection.

RESULTS OF SAMPLING AND ANALYSIS OF UNSATURATED-ZONE WATER

Table 1 presents the results of averaged duplicate analyses of water and trap samples collected by using four different methods from Picatinny Arsenal during July and September 1990. Measured TCE concentrations in the unsaturated-zone water ranged from less than 0.20 µg/L (micrograms per liter) to 500 µg/L, reflecting not only the effect of the variability caused by the sampling procedures, space, and time, but also the effect of a range of soil-moisture conditions and antecedent precipitation. The quantification limit for TCE is 0.2 µg/L. Concentrations less than 0.2 µg/L are reported in table 1 if the integration software used to analyze the chromatographic data could resolve a peak at the retention time for TCE. If no chromatographic peak could be resolved, ND is entered into table 1 to indicate that TCE was not detected. For statistical analysis of the data, a value of zero was assigned to the ND values in table 1. Although detectable concentrations less than 0.2 µg/L are not reliable, they have been included because they provide more information than a less than value for subsequent statistical analysis.

Table 1. *Mean trichloroethene concentration in water samples collected from suction lysimeters by four methods.*

[All concentrations in micrograms per liter; P&T, purge and trap; SYR, syringe; MBAT, modified Bengt-Arne Torstensson; STD, standard; --, no data available; ND, not detected]

		Sampling method			
Lysimeter	Sampling date (1990)	P&T method	SYR method	MBAT method	STD method
2-2	7/16	4.3	1.7	--	0.39
4-3	7/16	.48	2.6	--	.61
3-2	7/16	5.5	--	--	.24
2-3	7/17	.49	.26	--	.23
3-5	7/17	8.1	30.	--	27.
4-2	7/17	.15	.58	--	.16
4-5	7/18	.22	1.8	--	.14
5-4	7/18	.35	.22	--	.23
4-4	7/18	.04	1.3	--	.12
1-1	7/19	--	.57	--	1.3
3-1	7/19	--	43.	--	35.
4-1	7/19	--	2.7	--	.39
4-2	9/17	16.	.21	.09	.22
4-2	9/19	.75	2.0	ND	ND
2-2	9/19	--	--	.65	.50
3-1	9/19	500	--	430	98.
3-2	9/21	ND	ND	ND	ND
3-4	9/21	.68	.26	61.	ND
4-3	9/21	1.2	ND	ND	1.1
3-1	9/24	280	67.	61.	37.
4-4	9/24	.40	.70	.30	.14
2-5	9/24	77.	97.	35.	24.
2-5	9/26	93.	19.	27.	30.
3-1	9/26	160	32.	29.	21.
4-5	9/26	3.0	.20	.10	.22
2-5	9/28	55.	42.	50.	44.
3-1	9/28	130	61.	54.	46.
4-3	9/28	.26	.75	.47	.45

Samples collected with the MBAT method in July 1990 were analyzed by a different, nonstandard procedure relative to water samples collected with the SYR and STD methods. Therefore, these samples are not directly comparable with samples collected in September 1990 and were excluded from the data analyses. Samples collected with the P&T method on July 19, 1990, were not analyzed because of failure of the LSC 2000 purge-and-trap concentrator. In all other cases of missing data in table 1, insufficient flow rates of water from the lysimeter prevented collection of the sample.

The results in table 1 were analyzed with a two-sided Wilcoxon matched-pairs signed-rank test (Daniel, 1978). Each method was compared to each of the three remaining methods for a total of six two-sided tests. The null hypothesis of each test is that the median TCE concentration (measured by using the two methods being compared) are equal.. The alternate hypothesis is that the median concentrations are not equal. The test compares two methods by ranking the absolute values of the differences between pairs of data. The ranks corresponding to positive differences are summed, and the ranks corresponding to negative differences are summed. The smaller of these two sums is the test statistic. The sample size, *n*, is the number of nonzero differences between pairs of data. If the test statistic is relatively small for a given value of *n* and a desired confidence level, the null hypothesis is rejected. If the test statistic is relatively large, the null hypothesis is accepted.

With 95 percent confidence ($p = 0.05$), the SYR, P&T, and MBAT methods all resulted in higher median TCE concentrations than the STD method. The P&T method also resulted in a higher median TCE concentration than the MBAT method ($p = 0.05$). No statistically significant difference was found between the median concentration measured with the P&T and SYR methods or between the SYR and MBAT methods, even at a 90-percent confidence level ($p = 0.10$).

The precision and accuracy of the SYR and STD methods were determined in the laboratory by collecting 10 replicate samples from an aqueous solution with a TCE concentration of 20 µg/L. The average percent recoveries with 95-percent conifidence intervals for the SYR and STD methods are 106.5±5.0 and 84.4±5.8, respectively. Wood and others (1981) reported the average percent recovery for the P&T method is 103±9.8 with 95 percent confidence limits for an aqueous solution with a TCE concentration of 141 mg/L.

CONCLUSIONS

Results of the statistical analysis of concentration data for the four unsaturated-zone water sampling methodologies indicate that collection of water samples from the vadose zone for quantitative TCE analysis using both the P&T and SYR methods yields more accurate concentration values than collection using the MBAT or STD methods. This conclusion is based partly on the assumption that the statistically higher TCE concentrations observed in the field with the P&T and SYR methods relative to the MBAT and STD methods correspond to improved accuracy. The conclusion is supported directly by the high TCE recoveries reported for the SYR and P&T methods in the laboratory relative to the recovery reported for the STD method.

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SIMULATION OF GROUND-WATER FLOW AT PICATINNY ARSENAL, NEW JERSEY

By Lois M. Voronin[1]

ABSTRACT

Ground-water flow in the glacial sediments and bedrock at Picatinny Arsenal was simulated with a quasi-three-dimensional, finite-difference ground-water-flow model. Geophysical logs, lithologic logs, particle-size data, and test cuttings from selected wells were analyzed to identify six permeable layers and five intervening, low-permeability layers for simulation purposes.

Results of ground-water-flow simulation indicate that flow directions change in response to seasonal fluctuations in recharge rates. When ground-water-recharge rates are high, simulated flow in the water-table aquifer in the area of Building 24 at the arsenal is toward Green Pond Brook with a downvalley component, and ground water flows toward the arsenal at the southern boundary. When recharge rates are low, simulated flow in the water-table aquifer in the area of Building 24 is toward Green Pond Brook, but has a slight downvalley component; simulated ground-water flow in the water-table aquifer at the arsenal's southern boundary is away from the arsenal and downvalley to Rockaway River. These simulated ground-water-flow directions suggest the possibility of advective movement of contaminants in these areas.

Results of particle tracking analysis indicate that the distribution of trichloroethylene in the Building 24 area is not exclusively controlled by flow paths in the upper part of the unconfined aquifer, even when apparent dispersion caused by seasonal variations in the flow paths is considered. The difference between flow paths in the permeable layers in the upper and lower parts of the unconfined aquifer also affects the distribution of contaminants in the Building 24 area.

Based on calculated ground-water velocities near the Building 24 area, a conservative solute would be flushed from the ground-water system in approximately 250 to 550 days; however, contaminant concentrations in observation wells located in a contaminant plume near Building 24 have remained constant since the source was removed in 1985. Therefore, processes other than advective movement are involved with the transport of contaminants at this site.

INTRODUCTION

Picatinny Arsenal, located in Morris County, N.J. (fig. 1), has been a site of explosives manufacture since the mid-1880's and in 1908 became a research and development center for armaments. As a consequence of these activities, ground water at the arsenal is contaminated with several chlorinated organic compounds, including trichloroethene (TCE) near Building 24 (Fusillo and others, 1987). In order to describe the ground-water-flow system, which determines, in part, the extent and distribution of the contamination, a regional ground-water-flow model was constructed. A regional understanding of the ground-water-flow system at Picatinny Arsenal will aid in the study of the TCE plume near Building 24 and the possible movement of contaminants off the arsenal at the southern boundary (fig. 1). Simulated flows and calibrated hydraulic parameters from the regional flow model are being used in a solute-transport model of the Building 24 area at the site.

The purpose of this study was to define the ground-water flow system and provide a tool which could be used to predict the advective movement of conservative solutes at Picatinny Arsenal.

This paper presents the results of the simulation of ground-water flow at Picatinny Arsenal, with emphasis on the area of Building 24.

GROUND-WATER-FLOW SYSTEM

Picatinny Arsenal is located in the New Jersey Highlands, a northeast-southwest-trending system of rocks that form a sequence of valleys and ridges. The valleys are covered by a mantle of glacial sediments that range in thickness from 91 ft (feet) near Lake Picatinny to 185 ft at the southern boundary of Picatinny Arsenal.

Ground-water flow in the glacial sediments and bedrock at Picatinny Arsenal is controlled by the distribution of ground-water recharge, the location of streams, and the permeability of the bedrock and glacial sediments. The principal source of ground water to this region is local precipitation. The low permeability and steep slopes of Green Pond Mountain and Copperas Mountain restrict the infiltration of precipitation. Most of the precipitation that falls on the mountains flows overland to their bases and into the highly permeable glacial sediments. The small amount of precipitation that enters the bedrock of Green Pond Mountain and Copperas Mountain flows down through shallow fractures to the glacial sediments in the valley. Eventually, all of the precipitation that is not lost to the atmosphere through evapotranspiration flows to Rockaway River, Green Pond Brook, or other local surface-water bodies as overland flow or as ground-water discharge.

DESIGN OF GROUND-WATER-FLOW MODEL

A finite-difference ground-water-flow model (McDonald and Harbaugh, 1983) was used to simulate ground-water flow in the glacial sediments and bedrock at Picatinny Arsenal. A quasi-three-dimensional approach was employed. A finite-difference grid with 36 rows and 95 columns was used to discretize the model layers. The grid spacing is variable, ranging from 70 to 800 ft with cell size ranging from 5,600 to 320,000 square feet. Grid spacing near the Building 24 site ranges from 5,600 to 10,000 square feet.

For the purposes of simulation, the bedrock and glacial sediments at Picatinny Arsenal were divided into a sequence of six permeable layers and five intervening, low-permeability layers on the basis of the general hydraulic

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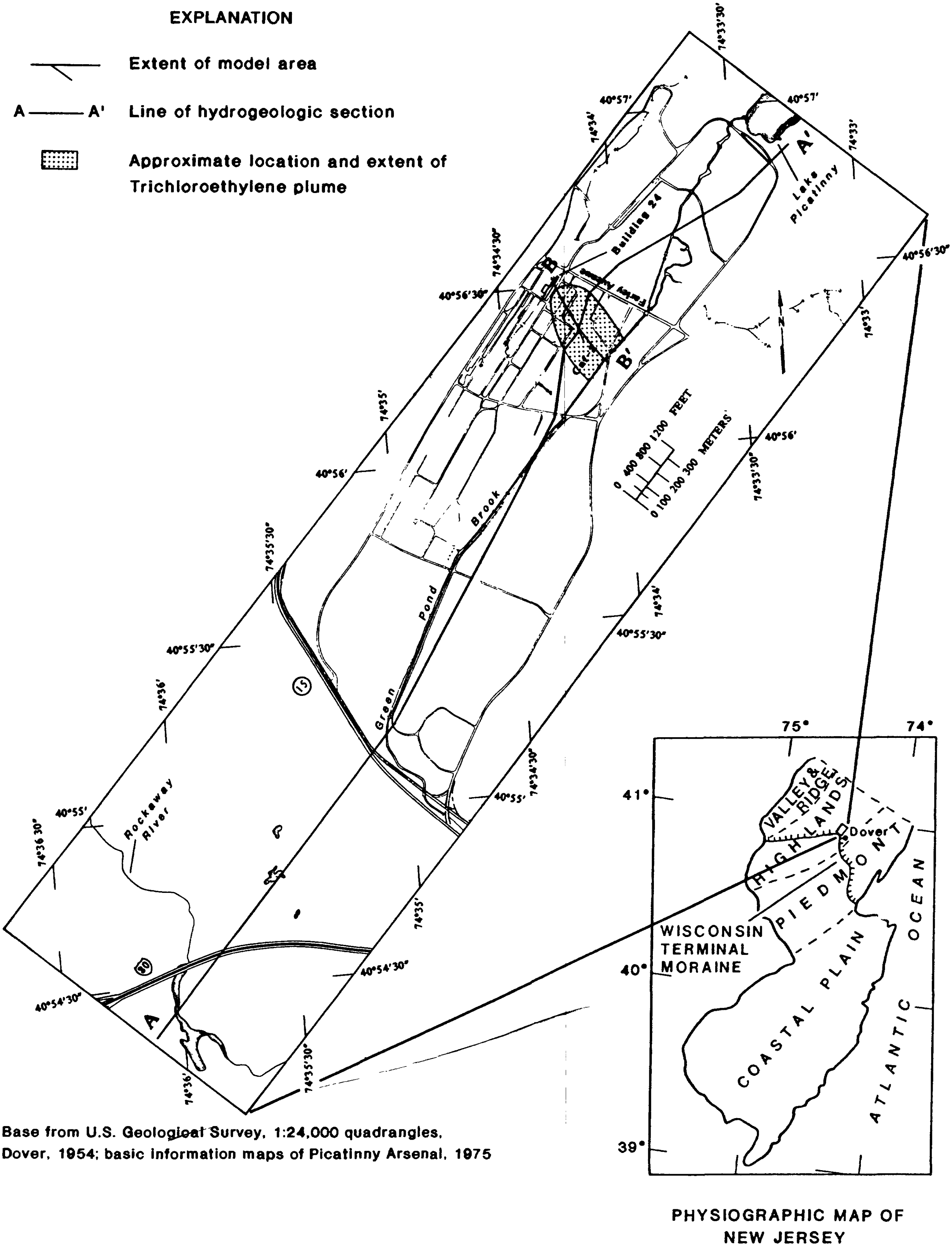
[1] U.S. Geological Survey, West Trenton, N.J.


EXPLANATION
Extent of model area
A —— A' Line of hydrogeologic section
Approximate location and extent of Trichloroethylene plume
A
A'
B
B'
Building 24
Lake Picatinny
Green Pond Brook
Rockaway River
15
80
N
0 400 800 1200 FEET
0 100 200 300 METERS
40°57'
40°56'30"
40°56'
40°55'30"
40°55'
40°54'30"
74°33'30"
74°33'
74°34'
74°34'30"
74°35'
74°35'30"
74°36'
74°36'30"
75°
74°
41°
40°
39°
VALLEY & RIDGE
HIGHLANDS
Dover
PIEDMONT
WISCONSIN TERMINAL MORAINE
COASTAL PLAIN
ATLANTIC OCEAN
PHYSIOGRAPHIC MAP OF NEW JERSEY

Base from U.S. Geological Survey, 1:24,000 quadrangles, Dover, 1954; basic information maps of Picatinny Arsenal, 1975

Figure 1. Location of study area.

properties of the sediments. Permeable sand units thicker than 10 ft were identified as the probable pathways for contaminants and therefore were designated as permeable layers. Confining units, such as thick clay layers, do not appear to be present at Picatinny Arsenal; however, layers that contain clay and(or) silt that impedes the flow of ground-water are present. The permeable layers consist of gravel, sand, and, in some locations, silt. The hydrogeologic units shown in figures 2 and 3 were determined from the analysis of 24 gamma-ray logs, 30 test cuttings, particle-size data, and 30 lithologic logs of selected wells at Picatinny Arsenal. Most of these data were collected in the area near the TCE plume near Building 24. The altitude of the bedrock surface was modified from Stanford (1989).

Calibrated horizontal hydraulic conductivities derived from the model for the permeable layers range from 10 to 500 ft/d (feet per day). Calibrated vertical hydraulic conductivities derived from the model for the low-permeability layers range from 0.01 to 0.5 ft/d. Calibrated horizontal hydraulic conductivities in the area of Building 24 range from 60 to 360 ft/d, and average about 220 ft/d.

The upper model boundary (the water table) includes areally distributed recharge, constant heads at Lake Picatinny (the northeastern part of the model area) and Rockaway River (the southwestern part of the model area). The lateral boundaries in the lower part of the glacial sediments at Lake Picatinny and Rockaway River are no-flow boundaries. Ground-water flow from upvalley is assumed to discharge to Rockaway River. Along the valley walls (the northwestern and southeastern parts of the model area) where the glacial sediments pinch out, fluxes vary with the amount of precipitation and with depth. A small amount of flow from the bedrock to the glacial sediments at the valley wall was assumed to occur. The lower boundary, the bottom of the fractured bedrock, is a no-flow boundary. The thickness of the permeable fractured bedrock aquifer was assumed to be 300 ft.

Ground-water levels at Picatinny Arsenal fluctuate as much as 8 ft as a result of variations in recharge rates. In order to simulate the fluctuation in water levels, the recharge rate was varied temporally in time intervals of 2 months to simulate transient conditions for the period 1981-89. The model was calibrated by matching water-level hydrographs of 17 wells from April 1983 through April 1989 and 168 water levels measured in April 1983, August 1983, and April 1989. All of the 168 measured water levels used for calibration were simulated to within 8 ft of the observed values; 82 percent of the 168 measured water levels were simulated to within 3 ft of observed values. In another transient simulation of two aquifer tests near Building 24, simulated drawdowns were matched to the drawdowns that were measured in observation wells during the tests.

Simulated recharge rates for 1981-89 were estimated from precipitation and base-flow data. Ground-water recharge was assumed to be equal to ground-water discharge to streams, and loss to withdrawals and downvalley flow out of the area was assumed to be negligible. Monthly ground-water discharge to Green Pond Brook was calculated by the streamflow-hydrograph-separation method from 7 years of discharge measurements for Green Pond Brook. From 1981-89, the maximum ground-water recharge rate was 8.5 in. (inches) per month, in March and April 1983; the minimum recharge rate was 0.2 in. per month, in August and September 1983.

SIMULATION OF GROUND-WATER FLOW

The TCE plume in the area of Building 24 extends downward into permeable layers 1, 2, and 3. These three permeable layers comprise the water-table aquifer described by Fusillo and others (1987, p 5). Therefore, only ground-water flow in permeable layers 1, 2, and 3 are discussed in this report.

Seasonal fluctuations in ground-water recharge have a significant effect on the direction of ground-water flow. Map A of figure 4 shows the simulated potentiometric surface for permeable layer 1, April 1983, a time of relatively high ground- water recharge and high ground-water levels. In the area of Building 24, ground-water flow is toward Green Pond Brook with a downvalley component. Near Route 15, at the southern boundary of the arsenal, ground-water flow in permeable layer 1 is toward the arsenal, Green Pond Brook, and a small pond.

Map B of figure 4 shows the simulated potentiometric surface for permeable layer 1 in August 1983, a time of relatively low ground-water recharge and low ground-water levels. Ground-water flow near Building 24 is toward Green Pond Brook, but has a slight downvalley component not present in the simulated April 1983 potentiometric surface. Ground-water flow at the southern boundary is away from the arsenal and down the valley toward Rockaway River.

Map C of figure 4 shows the simulated potentiometric surface for permeable layer 1 in April 1989, a period of average precipitation and ground-water recharge rate. Ground-water flow near Building 24 is toward Green Pond Brook, with a slight downvalley component. Ground-water-flow directions in the area of Building 24 during periods of average ground-water recharge resemble those observed during periods of low ground-water levels, whereas ground-water-flow directions at the southern boundary of permeable layer 1 during periods of average precipitation resemble those observed during periods of high ground-water levels.

The TCE contaminant plume near Building 24 follows the general direction of the flow paths simulated in layer 1, however, the central axis of the plume is upvalley from the flow paths shown in figure 4. These results indicate that the distribution of TCE in the Building 24 area is not exclusively controlled by flow paths in the upper part of the unconfined aquifer, even when apparent dispersion caused by seasonal variations in the flow paths is considered.

Directions of ground-water flow in permeable layers 2 and 3 are similar. Simulated potentiometric contours for permeable layer 3 in April 1983, August 1983, and April 1989 are shown in figure 5. Ground-water flow in the area of Building 24 in April 1983 (fig. 5, map A) is toward Green Pond Brook, with an upvalley component not present in the unconfined permeable layer 1. Ground-water flows during August 1983 and April 1989 (fig. 5, maps B and C) show similar directions to those seen in April 1983. Ground-water flow at the southern boundary of the arsenal in April 1983, August 1983, and April 1989 is down the valley and toward Rockaway River.

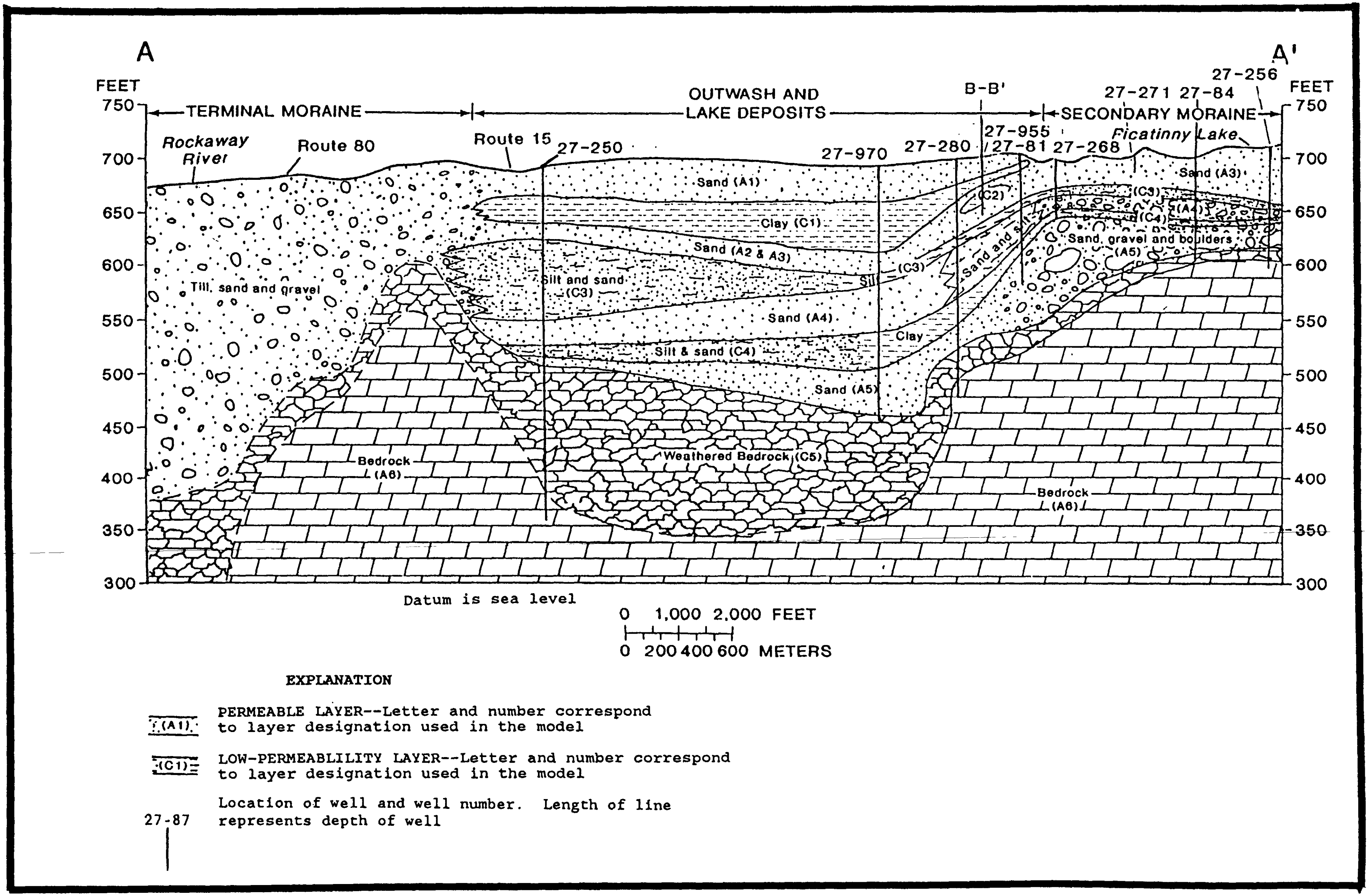
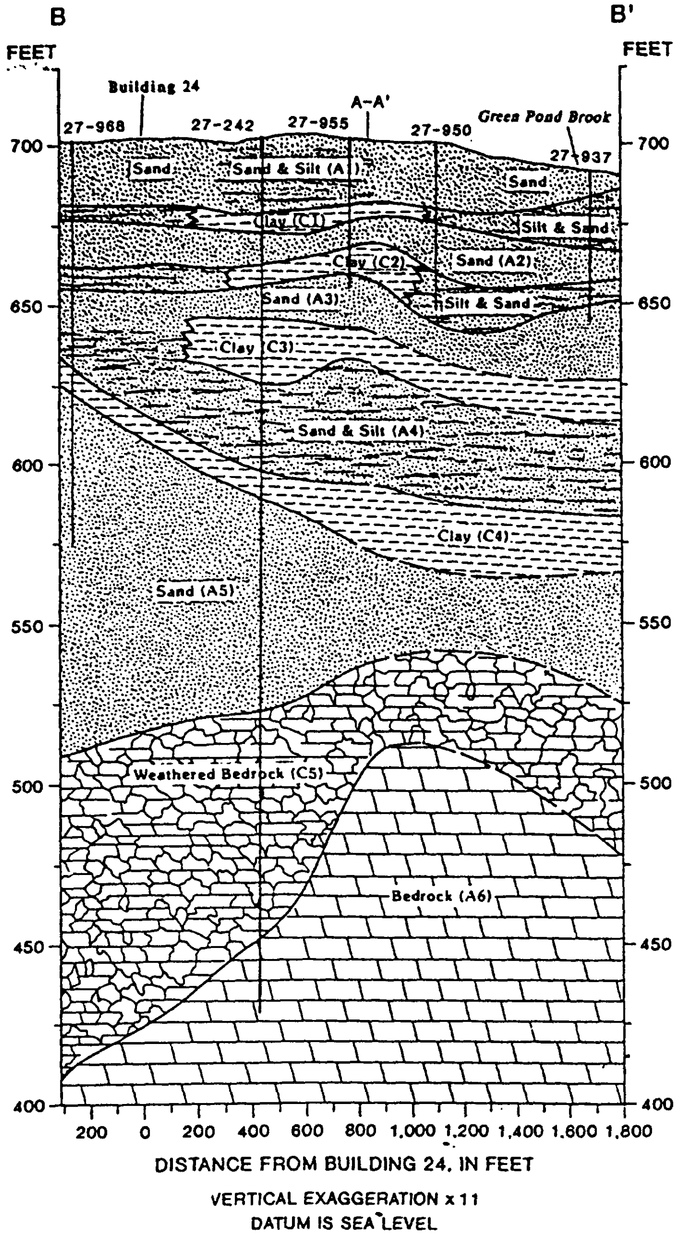

A
A'
FEET
750
700
650
600
550
500
450
400
350
300
TERMINAL MORAINE
OUTWASH AND LAKE DEPOSITS
SECONDARY MORAINE
B-B'
Rockaway River
Route 80
Route 15
27-250
27-970
27-280
27-955
27-81
27-268
27-271
27-84
27-256
Picatinny Lake
Sand (A1)
Clay (C1)
Sand (A2 & A3)
Silt and sand (C3)
Silt
(C3)
(C2)
Sand and silt
Sand (A4)
Clay
Silt & sand (C4)
Sand (A5)
Sand (A3)
(C3)
(A4)
(C4)
Sand, gravel and boulders
(A5)
Till, sand and gravel
Bedrock (A6)
Weathered Bedrock (C5)
Bedrock (A6)
Datum is sea level
0 1,000 2,000 FEET
0 200 400 600 METERS
EXPLANATION
(A1) PERMEABLE LAYER--Letter and number correspond to layer designation used in the model
(C1) LOW-PERMEABLILITY LAYER--Letter and number correspond to layer designation used in the model
27-87 Location of well and well number. Length of line represents depth of well

Figure 2. Hydrogeologic section A-A' (down the valley). (Location of section shown in fig. 1.)


B
B'
FEET
FEET
Building 24
A-A'
27-968
27-242
27-955
27-950
Green Pond Brook
27-937
Sand
Sand & Silt (A1)
Sand
Clay (C1)
Silt & Sand
Sand (A2)
Clay (C2)
Sand (A3)
Silt & Sand
Clay (C3)
Sand & Silt (A4)
Clay (C4)
Sand (A5)
Weathered Bedrock (C5)
Bedrock (A6)
700
650
600
550
500
450
400
200
0
200
400
600
800
1,000
1,200
1,400
1,600
1,800
DISTANCE FROM BUILDING 24, IN FEET
VERTICAL EXAGGERATION x 11
DATUM IS SEA LEVEL

EXPLANATION

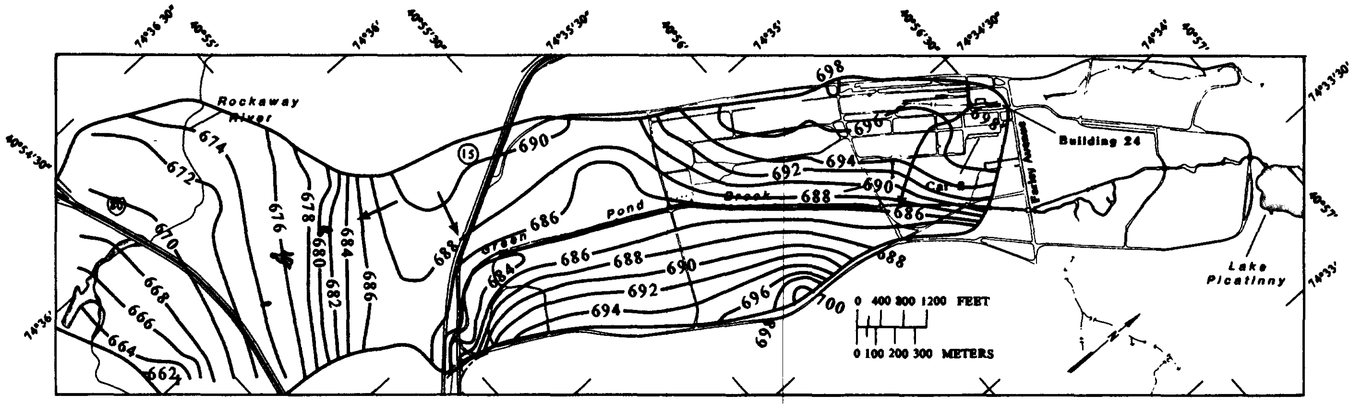
(A5) PERMEABLE LAYER--Letter and number correspond to layer designation used in the model

(C1) LOW-PERMEABLILITY LAYER--Letter and number correspond to layer designation used in the model

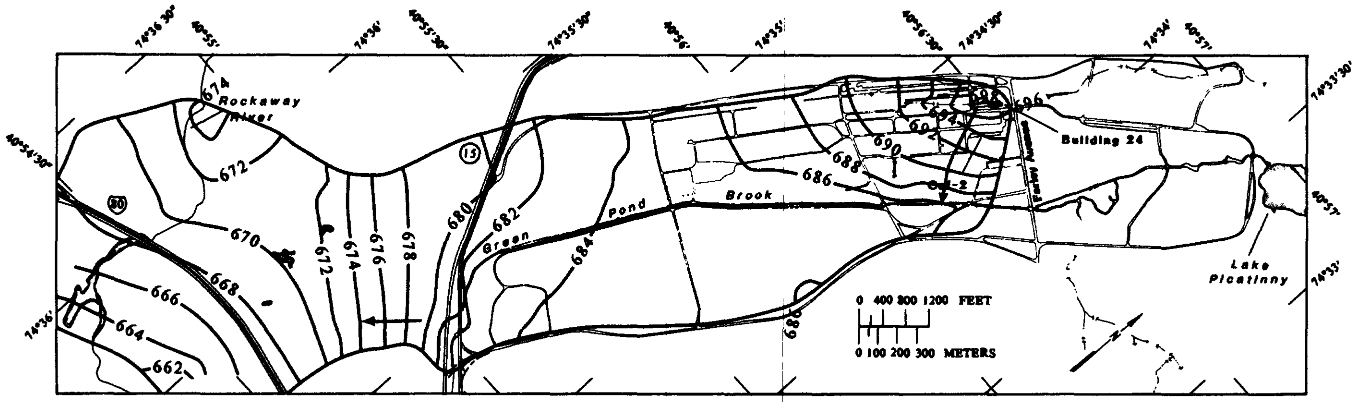
27-955 LOCATION OF WELL AND WELL NUMBER--Length of line represents depth of well

Figure 3. Hydrogeologic section B-B′ (across the valley). (Location of section shown in fig. 1.)

Map A.--Simulated April 1983 potentiometric surface


Rockaway River
Green Pond Brook
Building 24
Lake Picatinny
15
80
0 400 800 1200 FEET
0 100 200 300 METERS
662
664
666
668
670
672
674
676
678
680
682
684
686
688
690
692
694
696
698
700

Map B.--Simulated August 1983 potentiometric surface


Rockaway River
Green Pond Brook
Building 24
Lake Picatinny
15
80
0 400 800 1200 FEET
0 100 200 300 METERS
662
664
666
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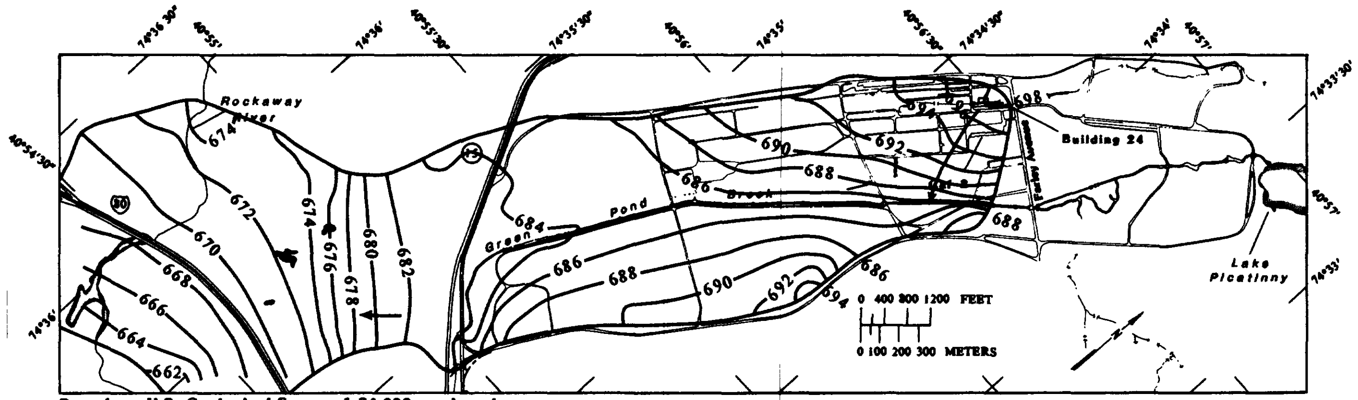
Map C.--Simulated April 1989 potentiometric surface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Base from U.S. Geological Survey, 1:24,000 quadrangles,
Dover, 1954; basic information maps of Picatinny Arsenal, 1975

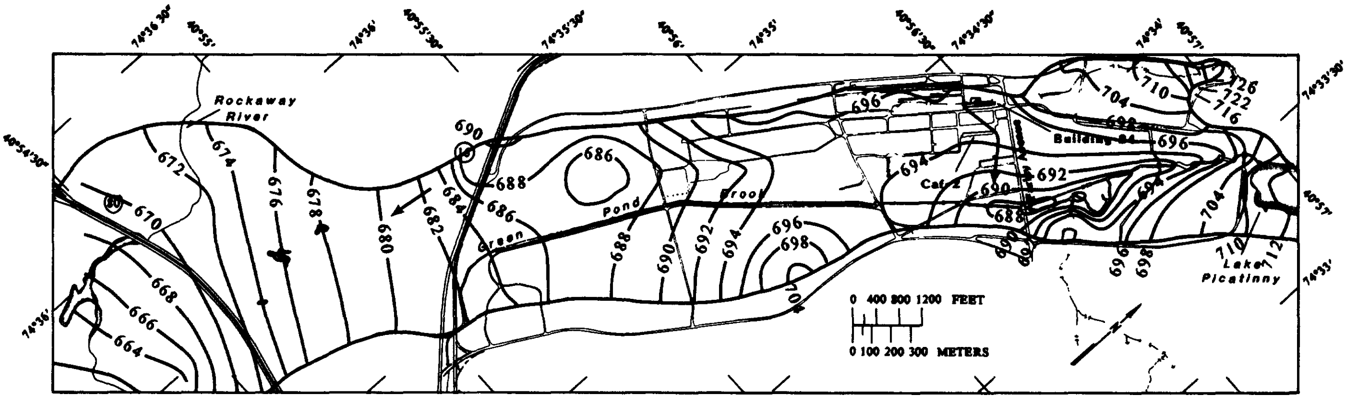
EXPLANATION

—670— SIMULATED POTENTIOMETRIC CONTOUR--Shows altitude of simulated potentiometric surface. Contour interval 2 feet. Datum is sea level

↙ General direction of ground-water flow

Figure 4. Simulated potentiometric surface for permeable layer 1, April 1983, August 1983, and April 1989.

Map A.--Simulated April 1983 potentiometric surface



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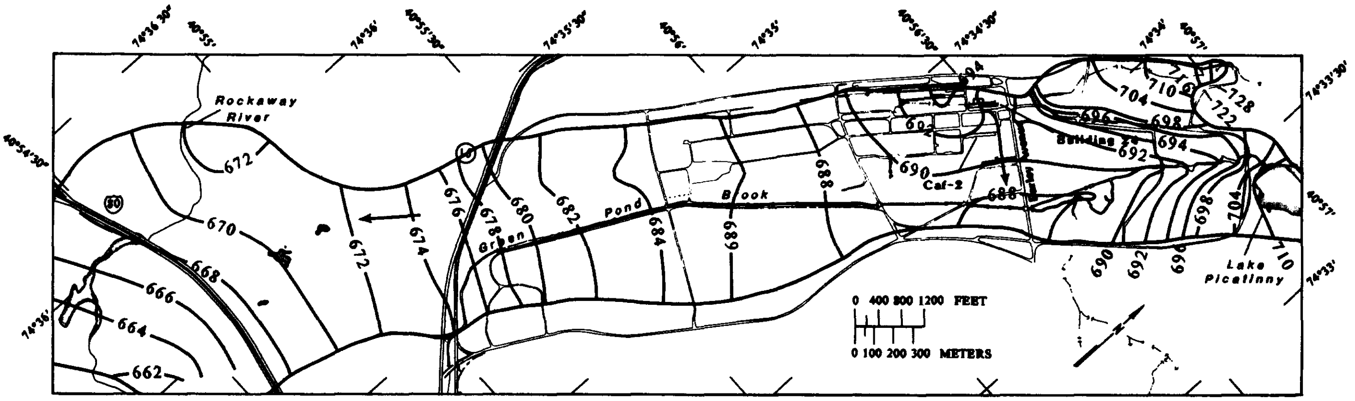
Map B.--Simulated August 1983 potentiometric surface



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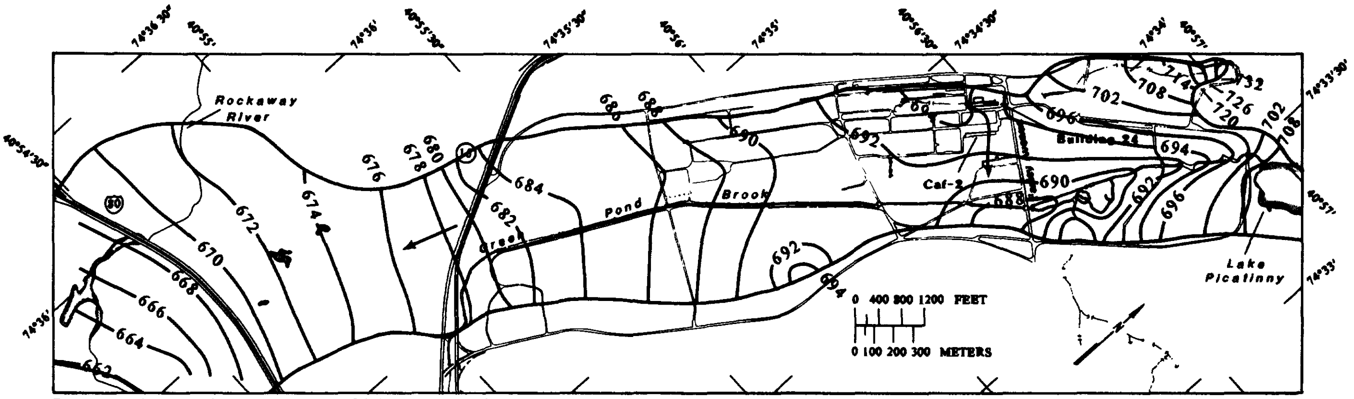
Map C.--Simulated April 1989 potentiometric surface



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0 100 200 300 METERS

Base from U.S. Geological Survey, 1:24,000 quadrangles,
Dover, 1954; basic information maps of Picatinny Arsenal, 1975

EXPLANATION

—690— SIMULATED POTENTIOMETRIC CONTOUR--Shows altitude of simulated potentiometric surface. Contour interval 2 and 6 feet. Datum is sea level

↙ General direction of ground-water flow

Figure 5. Simulated potentiometric surface for permeable layer 3, April 1983, August 1983, and April 1989.

The difference between flow paths in the permeable layers in the upper and lower parts of the unconfined aquifer is important in determining distribution of contaminants in the Building 24 area. Particle tracking, a post-processor to the flow model by Pollock (1989) shows that a conservative solute near Building 24 flows downward and slightly downvalley and then slightly upvalley toward Green Pond Brook. This flow path nearly coincides with the high TCE concentrations recently found near the bottom of the unconfined aquifer noted by Imbrigiotta and others (1991). This flow path is consistent with the observed distribution of contaminants which are further upvalley than is indicated by flow paths reflected by the water table.

Seasonal fluctuations in ground-water recharge rates also affect ground-water velocities. Ground-water velocities were calculated from water levels in a well approximately 10 ft from Building 24 (698.12 ft above sea level in April 1983, 692.14 ft above sea level in August 1983, and 695.78 ft above sea level in April 1989), a stream stage of 685 ft above sea level, an average horizontal hydraulic conductivity of 220 ft/d, and a porosity of 0.25. Calculated ground-water velocities between Building 24 and Green Pond Brook in April 1983 are 6.6 ft/d, whereas calculated ground-water velocities in the same area in August 1983 are 3.6 ft/d, and calculated ground-water velocities in the same area for April 1989 are 5.4 ft/d.

If only advective movement was involved with the transport of TCE near Building 24, it would take approximately 250 to 550 days (based on the above calculated ground-water velocities) to flush the TCE from the ground-water system (from Building 24 to Green Pond Brook). TCE concentrations in observations wells located in the TCE plume have remained constant since the source of the TCE was removed in 1985 (Imbrigiotta and others, 1991). Other processes are involved with the transport of TCE at this site.

SUMMARY AND CONCLUSIONS

Ground-water flow in the glacial sediments and bedrock at Picatinny Arsenal was simulated with a quasi, three-dimensional, finite-difference ground-water-flow model. The analysis of geophysical logs, lithologic logs, particle-size data, and test cuttings from selected wells was used to identify six permeable layers and five intervening low-permeability layers for simulation purposes.

Results of ground-water-flow simulation indicate that flow directions change in response to seasonal fluctuations in recharge rates. When ground-water-recharge rates are high, flow in the water-table aquifer in the area of Building 24 at the arsenal is toward Green Pond Brook with a downvalley component, and ground water flows toward the arsenal at the southern boundary. When recharge rates are low, flow in the water-table aquifer in the area of Building 24 is toward Green Pond Brook, but has a slight downvalley component. Ground-water flow in the water-table aquifer at the arsenal's southern boundary is away from the arsenal and downvalley to Rockaway River.

Results of particle tracking analysis indicate that the distribution of trichloroethylene in the Building 24 area is not exclusively controlled by flow paths in the upper part of the unconfined aquifer, even when apparent dispersion caused by seasonal variations in the flow paths is considered. The difference between flow paths in the permeable layers in the upper and lower parts of the unconfined aquifer also affects the distribution of contaminants in the Building 24 area.

Based on calculated ground-water velocities, it would take approximately 250 to 550 days to flush the TCE from the ground-water system. TCE concentrations in observations wells located in the TCE plume have remained constant since the source of the TCE was removed in 1985 (Imbrigiotta and others, 1991). Therefore, processes other than advective movement are involved with the transport of contaminants at this site.

A regional understanding of the ground-water-flow system at Picatinny Arsenal will aid in the study of a TCE contaminant plume at the site. Simulated flows and calibrated hydraulic parameters from the regional flow model are being used in a solute-transport model of the Building 24 area at the site.

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DESIGN OF A FIELD EXPERIMENT TO STUDY THE DYNAMICS OF TRICHLOROETHYLENE VAPORS IN THE UNSATURATED ZONE DURING AN INFILTRATION EVENT

By H. Jean Cho[1], Peter R. Jaffé[1], *and* James A. Smith[2]

ABSTRACT

Laboratory experiments are being conducted to examine the transport of volatile organic compounds in the unsaturated zone during infiltration. Measurements are being made of the concentration profile of trichloroethylene in soil air and soil water, and of the moisture profile within the soil. Preliminary data have shown that nonequilibrium phenomena are important in mass transport in two-phase (gas and water) laboratory soil systems during infiltration. A field experiment at Picatinny Arsenal in Morris County, New Jersey, is being planned to examine these processes on a field scale. When scaling an experiment from the laboratory to the field, natural spatial variability can be significant. Therefore, an examination of the variability in soil-water trichloroethylene concentrations in the field has been conducted. It has been found that spatial and temporal variability in soil-water concentrations are significant at Picatinny Arsenal, and that spatial variability is pronounced when sampling probes are located 1-meter from one another.

INTRODUCTION

Trichloroethylene (TCE) which has dissolved in ground water can be transported as a solute in the ground water, can sorb onto soil, and can volatilize into the soil-gas phase. In the soil-gas phase, TCE will diffuse upwards toward the land surface in response to natural concentration gradients.

In the absence of advective motion within an unsaturated porous medium, gas-phase transport of TCE can be modeled using Fick's laws of diffusion, modified to account for the tortuous path traveled by a molecule within a porous medium. Assumptions of thermodynamic equilibrium between the soil-water phase and the soil-gas phase are generally valid in nonadvective systems. However, in advective systems, such as a soil during infiltration of water or during soil-vapor extraction, the transport dynamics may be complex. For example, an ongoing laboratory column study of the dynamics of volatile organic compounds in the unsaturated zone has shown that soil-water-phase and soil-gas-phase TCE are not always in equilibrium during infiltration (Cho and Jaffé, 1990). Therefore, a numerical model of TCE transport in the unsaturated zone during infiltration requires a gas-water mass-transfer rate coefficient to simulate observed data.

As with all studies of the behavior of contaminants in the subsurface, the ultimate goal is to use the knowledge obtained in the laboratory to understand field situations. The complement to these laboratory experiments is a field infiltration experiment to be conducted at Picatinny Arsenal in Morris County, N.J. (fig. 1). To design and interpret such an experiment, the natural spatial variability of the field site must first be examined.

The objectives of this work are to (1) study spatial and temporal variations in soil-water TCE concentrations in the unsaturated zone at Picatinny Arsenal, and (2) use the knowledge of these variations to design a field infiltration experiment. The field experiment will examine the dynamics of gas-phase transport of TCE in the unsaturated zone during infiltration; we will compare the field results to laboratory results of the same phenomenon.

This paper reports the results of field experiments conducted in October 1990 at Picatinny Arsenal to examine spatial and temporal variability in soil-water TCE concentrations.

SUMMARY OF LABORATORY EXPERIMENTS

Column experiments are being conducted to determine whether gas- and aqueous-phase TCE in unsaturated sand columns is in equilibrium during infiltration (Cho and Jaffé, 1990). A reservoir of saturated TCE solution at the bottom of the sand column serves as the source of solute. Air at 100-percent relative humidity flows over the top of the sand column and exits through a carbon trap, thus maintaining a gas-phase TCE concentration of nearly zero at the soil surface. The infiltrating water is deionized.

Soil-water probes and soil-gas probes allow for measurement of the TCE concentrations in the two phases. Twenty-two pairs of these probes have been installed at 11 depths throughout the column, 2 pairs at each depth. In each pair, the gas probe is located 2 cm (centimeters) above the water probe so that soil-gas and soil-water concentration measurements can be made at approximately the same point in space. A tensiometer-transducer system measures soil matric head at the same 11 depths. The matric head can be converted to moisture contents using soil-moisture characteristic data.

In addition, net upward vapor fluxes are measured by analysis of the activated carbon from the carbon trap. The flux measurements are taken to verify the concentration measurements and the tortuosity.

Data from laboratory experiments conducted to date have been modeled by three solute-transport models. The first model used, the local equilibrium advective-dispersive model, proved inadequate at simulating the experimental data. During infiltration, the model predicted fluxes which were directly proportional to the dispersivity. In other words, the model predicted that the TCE was dissolving in the soil-water and being dispersed *upwards* in the downwardly flowing water phase.

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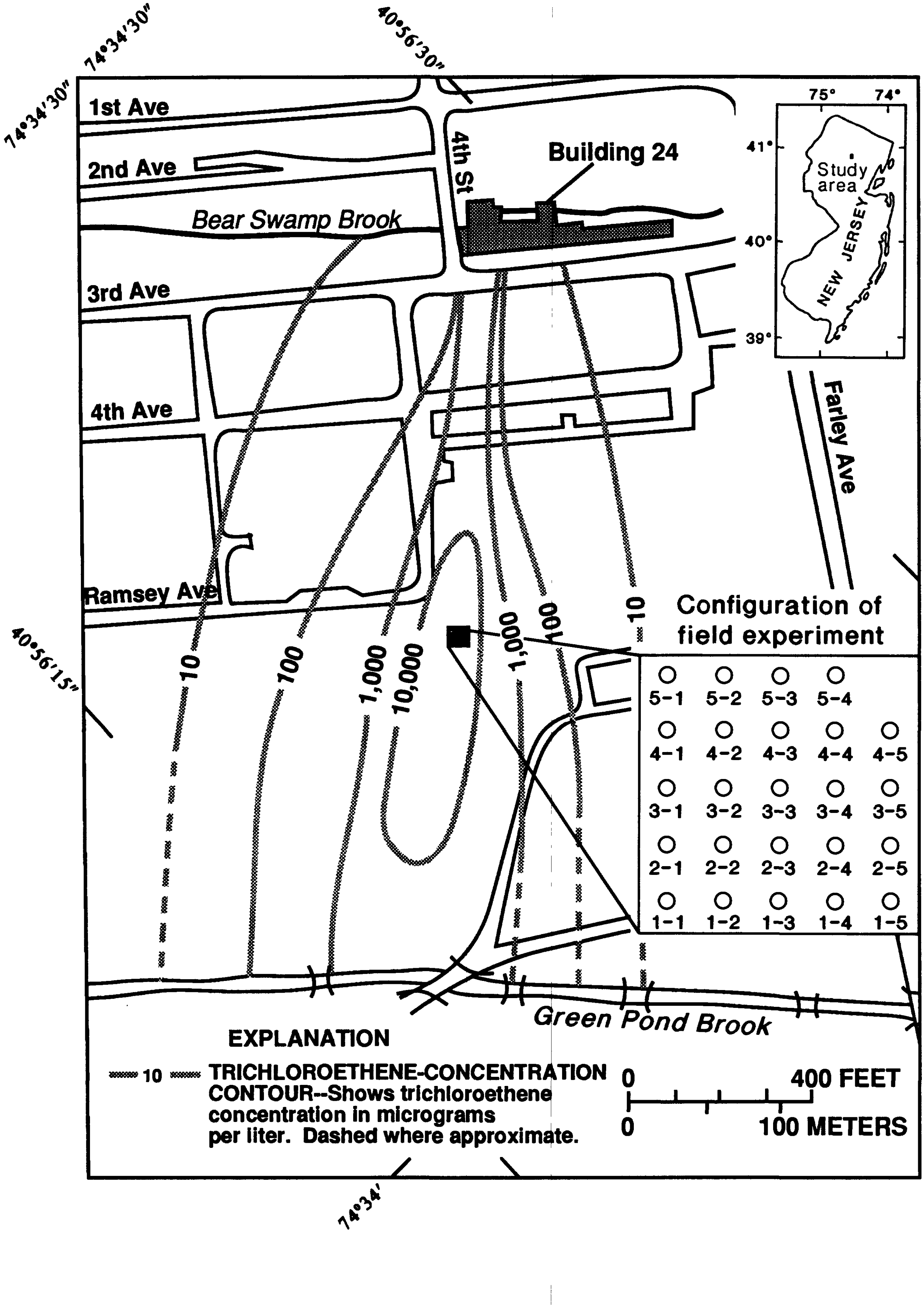
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Farley Ave
Green Pond Brook
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Configuration of field experiment
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2-1 2-2 2-3 2-4 2-5
1-1 1-2 1-3 1-4 1-5
EXPLANATION
10 TRICHLOROETHENE-CONCENTRATION CONTOUR--Shows trichloroethene concentration in micrograms per liter. Dashed where approximate.
0 400 FEET
0 100 METERS

Figure 1. Map of field site.

The second model, the nonequilibrium advective-dispersive model, incorporated a mass-transfer rate coefficient to describe interphase mass transfer between the phases. This second model predicted fluxes which increased with increased dispersivity, again suggesting that upward dispersion in the downwardly flowing water was an important transport pathway.

The dispersivity is a convenient means by which local variations in transport velocities can be modeled. Another method with which to incorporate velocity variations is the use of the mobile-immobile water-phase model, which assumes that a fraction of the water phase is mobile, whereas the rest of the water phase remains immobile (Coats and Smith, 1964; De Smedt and Wierenga, 1984).

The third model used to simulate the laboratory data was the nonequilibrium mobile-immobile water-phase model, which describes the unsaturated zone as a three-phase system--the soil-gas phase, the mobile soil-water phase, and the immobile soil-water phase. The third model was the simplest model to which the column data could be calibrated in a physically realistic manner. A more thorough discussion of the numerical simulations can be found in Cho and Jaffé (1990).

When soil gas and soil water are not in thermodynamic equilibrium, the concentration of TCE in one phase cannot be known merely from knowledge of the concentration of the other phase. Because of the coupled nature of the transport processes, soil-water and soil-gas concentrations must be measured in the field experiment for a full description of TCE dynamics. It is reasonable to assume that, over a distance of only a meter or so, soil-gas samples are rather homogeneous, because samples are averaged over a larger volume than the soil-water samples and because the diffusion coefficient of TCE in air is higher than its diffusion coefficient in water. The spatial variability of the concentration of TCE in soil water is unknown and, therefore, needs to be considered in the design of the field experiment. For this reason, preliminary field experiments, described below, were performed to test the spatial variability of soil-water samples.

FIELD EXPERIMENTS AT PICATINNY ARSENAL

Picatinny Arsenal is the site of a large TCE discharge dating from 1960, when TCE was the primary solvent used for metal degreasing. The wastewater from the degreasing operation was discharged into sand-lined lagoons and into an overflow dry well adjacent to Building 24 (fig. 1). The TCE has contaminated ground water in the unconfined aquifer and has migrated 500 m (meters) downgradient from the source to Green Pond Brook, the point of discharge for the aquifer system.

In 1988, soil-gas concentrations were measured in the unsaturated zone at Picatinny Arsenal. It was found that TCE from the plume at Picatinny Arsenal has volatilized into soil air and diffused to land surface (Smith and others, 1990). A maximum concentration of TCE of 7.3 µg/L (micrograms per liter) was found in the soil gas 30 cm above the water table adjacent to Building 24. Adjacent to the site chosen for the current experiments (fig. 1), a maximum concentration of 1.5 µg/L was found 30 cm above the water table.

As shown in figure 1, the field experiment will be conducted over the center of the plume. Therefore, relatively high concentrations of TCE in the unsaturated zone are expected, which will allow for ease of analysis. As in the laboratory experiment, soil-gas and soil-water concentrations will be measured at various depths. It is expected that soil-gas concentration measurements will be made using a 125-mL (milliliter) glass sampling bulb (Smith and others, 1990). Soil-water samples will be collected from the lysimeters with a vacuum and a 5-mL syringe as described by Smith and others (1991, this Proceedings).

To study the spatial variability of soil-water concentrations at the study area, a nest of 24 lysimeters were installed to a depth of 1.8 m below the land surface (fig. 1). They were installed in a square grid, with lysimeters spaced 1 m apart from each other. Details of the lysimeter installation are described in Smith and others (1991, this Proceedings).

The lysimeters were sampled on October 9, October 10, October 11, and October 15, 1990. Whenever possible, two samples were withdrawn from each lysimeter by the syringe method. Although it rained 1.1 cm the night before the October 9 samples were collected, the soil was relatively dry from at least 2 weeks of dry weather. Eight of the 24 lysimeters were sampled on October 9, but the sampling technique used was the modified BAT method because of an inadequate supply of 5-mL syringes for the syringe method on that day. The syringe method and the modified BAT method have been shown to be statistically equivalent. A description of these methods and a comparison of their effectiveness has been reported by Smith and others (1991, this Proceedings). Only five of the eight sampled lysimeters yielded enough water for two samples. No additional rainfall occurred before the samples were collected on October 10. The soil was relatively dry, and only 5 of the 24 lysimeters yielded water; only 3 of these 5 yielded 2 samples. A garden sprinkler was operated overnight before samples were collected on October 11. In addition, it rained 0.2 cm that night. On October 11, 10 of the 24 lysimeters were sampled, and 9 of them yielded 2 samples. The sprinkler was not used prior to sampling on October 15, but it rained 1.4 cm on October 12, and 3.8 cm on October 13, and the soil had remained moist from previous sprinkling. On October 15, eight lysimeters were sampled, and seven of them yielded two samples.

All of the samples collected on October 10, October 11, and October 15, 1990 were collected with a 5-mL syringe and analyzed by a Tracor 540 gas chromatograph with a Volcol capillary column and a Hall electrolytic conductivity detector. The samples collected on October 9 were collected in a 5-mL serum vial and capped with a Teflon-lined silicone septum. In the laboratory, the sample was transferred to a syringe and analyzed in the same manner as the syringe samples.

DISCUSSION OF PRELIMINARY FIELD RESULTS

A two-factor analysis of variance was performed on the soil-water samples obtained in the spatial variability experiment (Box and others, 1978). The two factors were

[3] The use of brand, firm, or trade names in this report is for identification purposes only and does not constitute endorsement by the U. S. Geological Survey.

the location of the lysimeter and the day of sampling. Table 1a shows the results of an analysis of variance for samples collected on October 9 and October 11, 1990. Only the lysimeters from which two samples were extracted on both days are analyzed. As mentioned above, the samples collected on October 9 were collected from a relatively dry soil, whereas the samples collected on October 11 were collected after application of water with a sprinkler as well as a natural rainfall. In addition, the samples collected on October 9 were collected with a different sampling technique. The effects of these factors can be seen in the analysis of variance table as well as in the incidence table. From the analysis of variance table, we see that there is only a 13-percent probability that, for a given lysimeter, the mean TCE concentration is the same for the 2 days. On the other hand, the difference between lysimeters is relatively slight, with a 90-percent probability that the mean TCE concentrations are identical for all three lysimeters on either day. However, it is evident from the incidence table (table 1b) that the difference in average measured concentrations between lysimeters (as opposed to total lysimeter means) is significant on both days. The results in table 1a indicate that, for this specific case, spatial variability is much less important than temporal variability.

Table 2a shows the corresponding results for samples collected on October 11 and October 15, 1990. The analysis of variance table shows a moderate probability (58 percent) that the mean soil-water concentrations at a given lysimeter did not change between the 2 days. On both of these days, the soil was relatively moist. However, the differences in lysimeters were pronounced. Soil-water concentrations from lysimeter 5-4 averaged 1.188 µg/L over the 2-day period, whereas concentrations from lysimeter 4-4, located 1 m away, averaged 0.373 µg/L.

These results indicate that spatial variability can be an important factor in the unsaturated soil-water concentrations at Picatinny Arsenal. When temporal changes (for example, variations in precipitation) are great, then the differences between lysimeters may be less important than the temporal variability, as shown in table 1a.

SUMMARY AND CONCLUSIONS

A series of laboratory experiments is being conducted to examine the transport and fate of a slightly water-soluble, volatile contaminant, TCE, in the unsaturated zone above a

Table 1a. *Analysis of variance table for lysimeters sampled on October 9, 1990 and October 11, 1990*

[η = number of replicates per sample; d = number of days; ℓ= number of lysimeters; t = index of days; s = index of lysimeters; ν = degrees of freedom; y = concentration; $\bar{y}$ = mean concentration]

Source of variation	Degrees of freedom	Sum of squares	Mean square	F-test ratio	P value
Between days	$\nu_d = 1$	$S_d = \eta\ell\sum_t^d(\bar{y}_t - \bar{y})^2 = 1.04$	$s_d^2 = S_d/\nu_d = 1.04$	$s_d^2/s^2 = 3.06$	0.131
Between lysimeters	$\nu_\ell = 2$	$S_\ell = \eta d\sum_s^\ell(\bar{y}_s - \bar{y})^2 = 0.070$	$s_\ell^2 = S_\ell/\nu_\ell = 0.035$	$s_\ell^2/s^2 = 0.102$	0.905
Residual	$\nu_{d\ell} = 2$	$S_{d\ell} = \eta\sum_t^d\sum_s^\ell(\bar{y}_{st} - \bar{y}_t - \bar{y})^2 = 0.542$	$s_{d\ell}^2 = S_d/\nu_{d\ell} = 0.271$	$s_{d\ell}^2/s^2 = 0.794$	0.494
Between replicates	$\nu = 6$	$S = \eta\sum_t^d\sum_s^\ell(y_{st} - \bar{y}_{st})^2 = 2.02$	$s^2 = S/\nu = 0.341$		

Table 1b. *Concentrations and concentration means for lysimeters sampled on October 9 and 11, 1990*

[In micrograms per liter]

	Lysimeter 4-2		Lysimeter 4-3		Lysimeter 5-4		**Daily mean ($\bar{y}_t$)**
	Raw data	**Mean**	Raw data	**Mean**	Raw data	**Mean**	
October 9:							
Sample 1	1.32		0.14		0.64		
Sample 2	0.25		0.64		0.73		
Sample mean ($\bar{y}_{st}$)		**0.79**		**0.39**		**0.69**	**0.62**
October 11:							
Sample 1	0.72		2.29		1.41		
Sample 2	0.96		0.68		1.20		
Sample mean ($\bar{y}_{st}$)		**0.84**		**1.49**		**1.31**	**1.21**
Lysimeter mean ($\bar{y}_s$)		**0.81**		**0.94**		**1.00**	**Grand mean ($\bar{y}$) 0.92**

Table 2a. *Analysis of variance table for lysimeters sampled on October 11, 1990 and October 15, 1990*

[η = number of replicates per sample; d = number of days; ℓ = number of lysimeters; t = index of days; s = index of lysimeters; ν = degrees of freedom; y = concentration; $\bar{y}$ = mean concentration]

Source of variation	Degrees of freedom	Sum of squares	Mean square	F-test ratio	P value
Between days	$\nu_d = 1$	$S_d = \eta\ell\sum_t^d(\bar{y}_t - \bar{y})^2 = 0.023$	$s_d^2 = S_d/\nu_d = 0.330$	$s_d^2/s^2 = 3.30$	0.581
Between lysimeters	$\nu_\ell = 3$	$S_\ell = \eta d\sum_s^\ell(\bar{y}_s - \bar{y})^2 = 1.62$	$s_\ell^2 = S_\ell/\nu_\ell = 0.539$	$s_\ell^2/s^2 = 7.91$	0.009
Residual	$\nu_{d\ell} = 3$	$S_{d\ell} = \sum_t^d\sum_s^\ell(\bar{y}_{st} - \bar{y}_t - \bar{y}_i + \bar{y})^2 = 0.102$	$s_{d\ell}^2 = S_d/\nu_{d\ell} = 0.034$	$s_{d\ell}^2/s^2 = 0.501$	0.692
Between replicates	$\nu = 8$	$S = \sum_t^d\sum_s^\ell(y_{st} - \bar{y}_{st})^2 = 0.545$	$s^2 = S/\nu = 0.068$		

Table 2b. *Concentrations and concentration means for lysimeters sampled on October 11 and 15, 1990*

[In micrograms per liter]

	Lysimeter 2-2		Lysimeter 4-4		Lysimeter 4-5		Lysimeter 5-4		**Daily mean ($\bar{y}_t$)**
	Raw data	**Mean**	Raw data	**Mean**	Raw data	**Mean**	Raw data	**Mean**	
October 11:									
Sample 1	0.33		0.38		0.98		1.41		
Sample 2	0.55		0.28		0.88		1.20		
Sample mean ($\bar{y}_{st}$)		**0.44**		**0.33**		**0.93**		**1.31**	**0.75**
October 15:									
Sample 1	0.57		0.60		0.32		1.33		
Sample 2	0.48		0.23		1.07		0.81		
Sample mean ($\bar{y}_{st}$)		**0.52**		**0.42**		**0.70**		**1.07**	**0.68**
Lysimeter mean ($\bar{y}_s$)		**0.48**		**0.37**		**0.81**		**1.19**	**Grand mean ($\bar{y}$) 0.71**

contaminated unconfined aquifer. Measurements of soil-gas and soil-water concentrations are used to determine the applicability of equilibrium models and to calibrate mass-transfer rate coefficients as needed. From experiments conducted to date, it appears that the nonequilibrium mobile/immobile water-phase model is the most consistent and realistic model for simulating the laboratory experiments.

A field infiltration experiment is being planned to study the transport of volatile compounds under natural conditions. In preparation for the infiltration experiment, an experiment was conducted to examine spatial and temporal variability. This experiment has shown that, when significant changes in precipitation occur, temporal changes in soil-water concentration are significant. Therefore, we expect that an experiment conducted to examine the temporal response of soil-water concentration during infiltration will lead to interesting and useful results.

When significant changes in precipitation do not occur, however, the spatial variability of soil-water concentrations is important. Significant soil-water concentration variations were observed in probes located 1 m apart and at the same depth. Because spatial variability in soil-water concentrations can be significant, it is desirable that soil-gas and soil-water concentrations be collected from the same spatial point. Therefore, at each depth at which samples are to be collected, the soil-water probe will be installed immediately adjacent to the soil-gas probe within the same borehole. The sampling sites will consist of boreholes in which pairs of probes (one for gas, one for water) will be installed at each of several depths.

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CHARACTERIZATION OF HIGH MOLECULAR WEIGHT, COLORED COMPOUNDS IN GROUND WATER AT PICATINNY ARSENAL, NEW JERSEY

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ABSTRACT

A zone of dark-colored ground water containing a high dissolved organic carbon content has been found in water from a well directly adjacent to a pipe that discharged chlorinated solvents directly into the unsaturated zone of the aquifer beneath the Picatinny Arsenal, New Jersey. The zone of colored water has moved from the point of discharge to a second well about 90 feet downgradient. Fulvic acids have been isolated from samples of the colored waters from both wells and from water from a background well that has not been affected by the discharge of chlorinated solvents. The nuclear magnetic resonance spectra of the fulvic acids from the colored waters are very similar, but are markedly different from the nuclear magnetic resonance spectrum of the fulvic acid from the background well. It has been tentatively concluded that the colored waters are soil pore waters that have been displaced by dense chlorinated solvents discharged into the unsaturated zone.

INTRODUCTION

Ground water downgradient from Building 24 at the Picatinny Arsenal Toxic Waste Hydrology research site has been found to contain trichloroethylene (TCE) and lesser amounts of other chlorinated solvents (Imbrigiotta and others, 1989; Sargent and others, 1990). Building 24 was the location of a degreasing and metal-plating operation for approximately 25 years. During 1973 to 1985, TCE was discharged from an overflow pipe from the degreasing unit to a 4-ft (foot)-deep dry well in front of the building. The infiltration of TCE from the dry well created a plume of TCE- contaminated ground water that extends from Building 24 to Green Pond Brook (fig. 1).

During ground-water sampling in October 1987, a zone of dark-colored ground water with a concentration of dissolved organic carbon (DOC) greater than 12 milligrams per liter was detected in a small number of wells immediately downgradient of Building 24. Subsequent sampling has shown that high DOC concentrations are still present in these wells. None of the other monitoring wells at the arsenal has yielded colored waters with high DOC concentrations.

This paper describes a study of the origin of this high-DOC water. From the data we have on the types of compounds that were discharged from the plating facility, there is no indication that colored DOC was discharged in the pollutant stream, which consisted mainly of TCE. In addition, it is highly unlikely that the colored DOC is produced by the degradation of TCE. The results of our investigation indicate that the most likely source of the DOC is the soil pore water.

SAMPLE COLLECTION

A water sample was collected in March 1988, from well E-2B-10. This sampling point, which is located 10 ft downgradient from the dry well (fig. 1) is a ¼-in.-(inch)diameter stainless-steel tube that is set to a depth of 10 ft below the land surface. In June 1990, well 9-E, 90 ft downgradient of the dry well and well 13-2, 345 ft upgradient of the dry well were sampled. Well 9-E is a 2-in. diameter stainless-steel pipe that is set to a depth of 19 ft below the land surface; well 13-2 is a 2-in-diameter polyvinylchloride pipe set to a depth of 20 ft below the land surface.

In all of the sampling, the wells were first pumped to flush them out. This pumping was continued until the specific conductance and pH of the water stabilized. A 10-gallon sample from well E-2B-10 was obtained with a peristaltic pump; this sample was chilled and shipped to the U.S. Geological Survey laboratory in Denver for further processing. Wells 9-E and 13-2 were pumped with a gear submersible pump. Approximately 794 L (liters) of water were collected from 13-2 and 113 L from 9-E; the humic substances from these samples were concentrated on site. The concentrates were shipped back to Denver for further processing.

EXPERIMENTAL PROCEDURES

Two different procedures were used to isolate the colored DOC from the ground water samples. The sample collected from well E-2B-10 in March 1988, was processed by a procedure developed by Leenheer and others (1989) to avoid the use of strongly basic solutions during any of the processing steps. Briefly, the sample was first concentrated to about one-quarter of its volume on a rotary evaporator. The sample was centrifuged to remove suspended colloidal material. The pH of the supernatant was adjusted to 2 with hydrochloric acid (HCl), and it was then placed on an XAD-8[3] column. The column was first eluted with a pH 2 HCl solution to remove the salts and hydrophilic organic acids from the column. This was followed by elution of the colored DOC (mainly fulvic acid) from the column with a solution that was 0.75 by volume acetonitrile, 0.25 by volume HCl. The column was then rinsed with a volume of water equal to about two-thirds the volume of the acetonitrile-HCl eluant. The water rinse was added to the acetonitrile-HCl eluant and the entire volume was taken to dryness on the rotary evaporator. The residue in the rotary evaporator flask was dissolved in a small volume of 0.75 acetonitrile/0.25 water solution and freeze dried.

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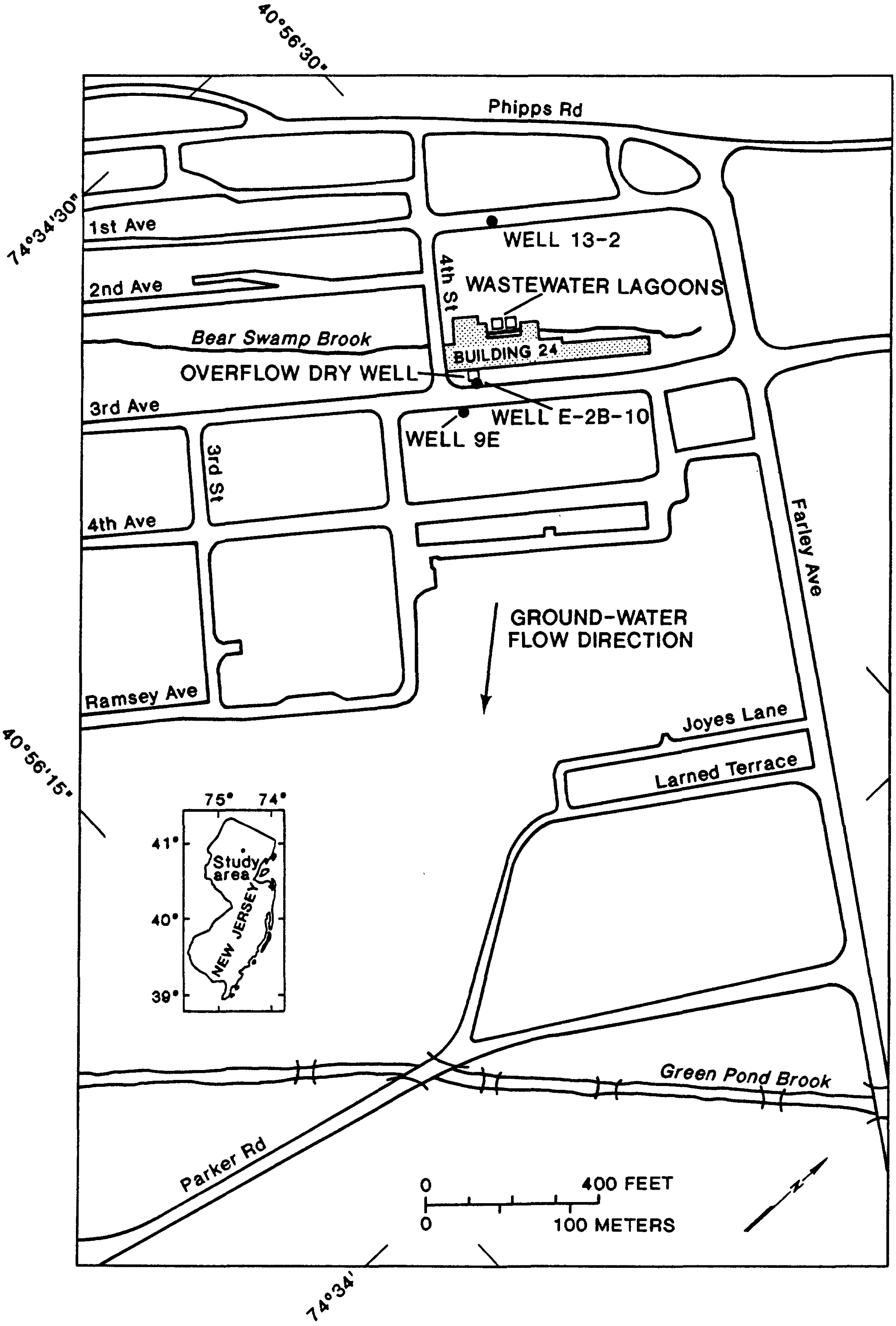
[3] The use of brand, firm, or trade names in this paper is for identification purposes only and does not constitute endorsement of the U.S. Geological Survey.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Phipps Rd
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WELL 13-2
2nd Ave
4th St
WASTEWATER LAGOONS
Bear Swamp Brook
BUILDING 24
OVERFLOW DRY WELL
3rd Ave
WELL E-2B-10
WELL 9E
3rd St
4th Ave
Farley Ave
GROUND-WATER FLOW DIRECTION
Ramsey Ave
Joyes Lane
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Larned Terrace
75°
74°
41°
Study area
NEW JERSEY
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Green Pond Brook
Parker Rd
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Figure 1. Location of sampling sites at Picatinny Arsenal, New Jersey.

The samples collected in June 1990, were processed by the procedure described by Thurman and Malcolm (1981). A brief outline of this procedure is given here. Unfiltered water was acidified to pH 2 with HCl in glass carboys and passed through an XAD-8 column. The fulvic acid retained on the XAD-8 column was back eluted from the column with 0.1N NaOH. The NaOH eluates were immediately acidified with concentrated HCl to pH 2 to minimize alteration of the sample at high pH. The eluates were reconcentrated on an XAD-8 resin column, H-saturated using AG-MP 50 cation-exchange resin, and lyophilized.

The nuclear magnetic resonance (NMR) spectra were measured on solutions of approximately 100 milligrams per milliliter of the sodium salt of each of the samples dissolved in H_2O-D_2O (3 parts to 1 part) mixtures in 10-millimeter diameter tubes on a Varian XL 300 spectrometer at 75.429 megahertz. Quantitative spectra were obtained using inverse gated-decoupling in which the proton decoupler was on only during the acquisition of the free induction decay curve (FID); an 8-second delay time and a 45 degree tip angle were used. The sweep width was either 30,000 Hz (hertz) or 50,000 Hz.

Elemental analyses were performed by Huffman Laboratories. A review of the methods used for the determination of each element has been published by Huffman and Stuber (1985).

RESULTS AND DISCUSSION

The carbon-13 (^{13}C) NMR spectra of humic substances generally consist of broad bands which occur in well-defined spectral regions. The positions (chemical shifts) of the major bands in all of the published ^{13}C NMR spectra of humic substances are remarkably similar (Wershaw and others 1990). The chemical shifts of the these bands allow one to determine what functional groups are present in a sample. We have divided the spectra into regions that are correlated to different categories of functional groups as listed in table 1. Because of the broadness of the bands in the ^{13}C NMR spectra of humic substances, it is not possible to be more specific in these spectral assignments. Integration of the areas under the bands in each of the spectral regions listed in table 1 provides a measure of the relative concentrations of the different types of functional groups present in the samples.

The NMR spectra of the fulvic acid isolates from the two wells downgradient of the TCE contamination and from the background well are given in figures 2 and 3. The NMR spectra of the fulvic acids from well E-2B-10 and from well 9-E are very similar. The relative concentrations of the functional groups in these samples obtained by spectral integration are given in table 2. As expected from the similarities in NMR spectra, the relative concentrations of functional groups in wells E-2B-10 and 9-E are very similar. The relative concentration of aliphatic functional groups is somewhat higher and the concentration of aromatic groups lower in the sample from E-2B-10 than the one from 9-E. These differences may have resulted from the differences in the isolation procedures used for the two samples.

Table 1. *Nominal positions of major bands in ^{13}C NMR spectra of humic substances*

[Chemical shifts are given in ppm (parts per million) from tetramethylsilane (TMS) resonance at 0]

Chemical shifts		Functional group carbons
0-62	ppm	Aliphatic carbons
62-90	ppm	Alcoholic carbons in carbohydrates
90-110	ppm	Anomeric carbons in carbohydrates
110-160	ppm	Aromatic carbons
160-190	ppm	Carboxylate carbons
190-230	ppm	Carbonyl carbons in aldehydes and ketones

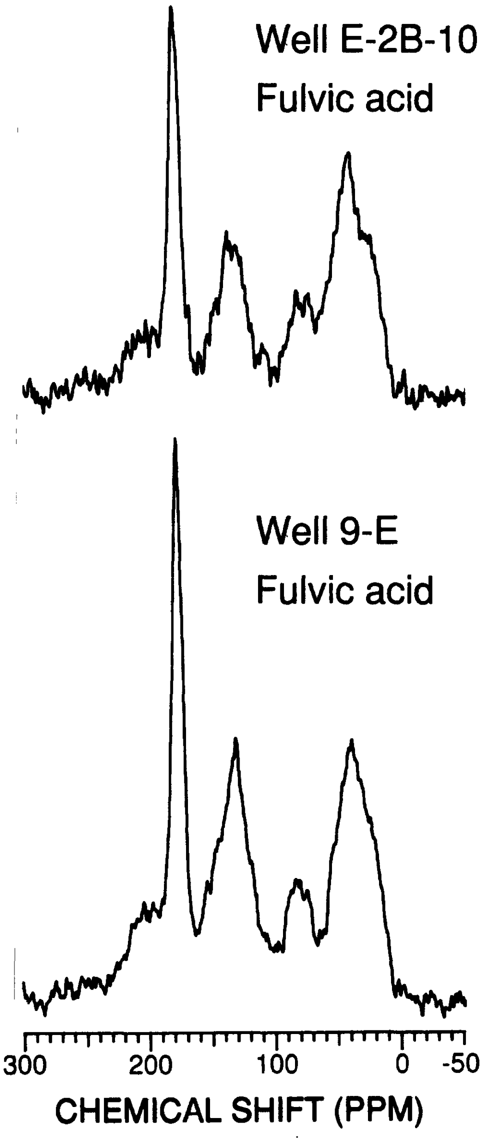

Figure 2. ^{13}C NMR spectra of fulvic acids isolated from wells downgradient from trichloroethylene contamination (wells E-2B-10 and 9-E). Chemical shift in parts per million (ppm) from tetramethylsilane at 0 ppm.