U.S. GEOLOGICAL SURVEY PROGRAM ON TOXIC WASTE—GROUND-WATER CONTAMINATION: PROCEEDINGS OF THE THIRD TECHNICAL MEETING, PENSACOLA, FLORIDA, MARCH 23-27, 1987

By Bernard J. Franks, Editor

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DONALD PAUL HODEL, Secretary

U.S. GEOLOGICAL SURVEY

Dallas L. Peck, Director

For additional information
write to:

Coordinator, Toxic Waste—
Ground-Water Contamination
Program
U.S. Geological Survey
410 National Center
Reston, Virginia 22092

Copies of this report can be
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U.S. Geological Survey
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FOREWORD

This is the third technical meeting of the U.S. Geological Survey's Toxic Waste—Ground-Water Contamination Program since the program's inception in fiscal year 1982. Over these years the meetings (in Tucson, Ariz., in March 1984; in Cape Cod, Mass., in October 1985; and now here in Pensacola, Fla., in 1987) serve to mirror the development of the program as a technical strategy for studying the effect of human activity on the Nation's ground-water resources.

It was perceived at the beginning of the program that no single scientific discipline or approach would succeed in the study of the interaction between mixtures of manmade organic and inorganic chemicals and the multiphase and multicomponent systems found in nature. The strategy that was formulated to address so complex an issue was to provide the opportunity for researchers from a variety of scientific disciplines to work at field sites where ground-water contamination had occurred. Three field sites were initially selected to study ground-water contamination: the infiltration of sewage-treatment effluent on Cape Cod, Mass.; a crude-oil pipeline break near Bemidji, Minn,; and the infiltration of creosote/pentachloraphenol through waste-disposal ponds near Pensacola, Fla. To implement the strategy, workplans were prepared in order to integrate and focus the studies of the individual researchers. Hypotheses were developed about the fate and transport of selected compounds in the plumes of contaminated ground water in order to better direct the research initiatives at the sites. The Tucson meeting provided the opportunity to bring the researchers together to discuss and evaluate the workplans. As such the meeting formalized and initiated the Toxic Waste Program.

The intensive fieldwork following the Tucson meeting provided much information about the hydrological and geochemical systems under study and the distribution of the contaminants in the subsurface. Many of the original hypotheses about the movement of contaminants through the subsurface were not supported by the new knowledge. Sampling and analytical methods of study were found wanting and in need of improvement. It is probably safe to say that the only notions not affected by the early work were that ground-water systems are complex and that plumes of contaminants are not easily characterized.

Another kind of experiment conducted at the field sites dealt with our ability to implement truly interdisciplinary studies. The experiment tested the resolve of scientists in the U.S. Geological Survey, from both the Water Resources Division and the Geologic Division, and from universities to work together and on problems of mutual interest. The Cape Cod meeting demonstrated that these experiments were proceeding successfully. Interdisciplinary research was found to be alive and thriving at the research sites.

The Cape Cod meeting provided the opportunity for researchers to exchange information gathered over the previous 18 months and to compare notes. Unlike the usual technical meeting, the Cape Cod meeting provided an integrated understanding of the research knowledge gained from work that focused on a particular earth-science problem. As a result of the meeting, additional investigations were integrated into the overall research program of the field sites.

The Pensacola meeting, the proceedings of which are the subject of this volume, demonstrates how well the technical strategy has developed. Much interdisciplinary research knowledge has been presented cooperatively by researchers in the U.S. Geological Survey, other Federal agencies, and from many universities. The results being presented are much more detailed than those presented at the two previous meetings. The extended abstracts represent the more detailed findings being reported in the literature as indicated in the bibliography at the end of this volume.

As the proceedings indicate, much study continues at the field sites. New initiatives have begun to make the scope of the research more comprehensive. Other studies have moved to the laboratory or to the computer. In some cases, other fieldwork has been initiated in order to expand the types of contaminants being investigated or to understand the transfer value of the information for similar compounds.

The technical strategy developed for the Toxic Waste Program seems to have merit. The knowledge and experiences gained and reported at these meetings should help us as we continue to resolve the earth-science issues critical to the problems of ground-water contamination in our Nation.

Steve Ragone

Stephen E. Ragone
Coordinator, Toxic Waste—Ground-Water
Contamination Program

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CONVERSION FACTORS

For the use of those readers who may prefer to use inch-pound units rather than International System (SI) units, the conversion factors for the terms used in this report are listed below.

Multiply SI unit	By	To obtain inch-pound unit
nanometer (nm)	3.937x10^{-8}	inch (in.)
micrometer (μm)	0.00003937	inch (in.)
millimeter (mm)	0.03937	inch (in.)
centimeter (cm)	0.3937	inch (in.)
centimeter per second (cm/s)	0.0328	foot per second (ft/s)
centimeter per day (cm/d)	0.0328	foot per day (ft/d)
centimeter per year (cm/yr)	0.0328	million feet per year (Mft/yr)
cubic centimeter (cm^3)	0.06102	cubic inch (in^3)
meter (m)	3.281	foot (ft)
	1.094	yard (yd)
meter per second (m/s)	3.281	foot per second (ft/s)
meter per day (m/d)	3.281	foot per day (ft/d)
meter per year (m/yr)	3.281	foot per year (ft/yr)
square meter per gram (m^2/g)	305.2158	square foot per ounce (ft^2/oz)
cubic meter (m^3)	35.31	cubic foot (ft^3)
	264.2	gallon (gal)
	1.308	cubic yard (yd^3)
cubic meter per second (m^3/s)	35.3145	cubic foot per second (ft^3/s)
	22.83	million gallons per day (Mgal/d)
kilometer (km)	0.6214	mile (mi)
square kilometer (km^2)	0.3861	square mile (mi^2)
milliliter (mL)	0.0338	ounce, fluid (oz)
milliliter per cubic centimeter (mL/cm^3)	0.5539	ounce per cubic inch (oz/in.^{3})
milliliter per gram (mL/g)	0.007491	gallon per ounce (gal/oz)
liter (L)	33.82	ounce, fluid (oz)
	2.113	pint (pt)
	1.0567	quart (qt)
	0.2642	gallon (gal)
	0.03531	cubic foot (ft^3)
liter per minute (L/min)	5.886x10-^{4}	cubic foot per second (ft^3/s)
liter per day (L/d)	0.03531	cubic foot per day (ft^3/d)
liter per month (L/mon)	0.03531	cubic foot per month (ft^3/mon)
liter per gram (L/g)	7.491	gallon per ounce (gal/oz)
hectare (ha)	2.471	acre
nanogram per gram (ng/g)	1.0000x10^{-9}	ounce per ounce (oz/oz)
nanogram per milliliter (ng/mL)	133.4974x10^{-9}	ounce per gallon (oz/gal)
microgram (μg)	0.00001543	grain (gr)
microgram per liter (μg/L)	0.00005841	grain per gallon (gr/gal)
microgram per gram (μg/g)	1.0000x10^{-6}	ounce per ounce (oz/oz)
microgram per square meter per second (μg/m^2)/s	0.003276x10^{-6}	ounce per square foot per second (oz/ft^2/s)

milligram (mg)	0.0000353	ounce (oz)
milligram per liter (mg/L)	1.0	parts per million (ppm)
	0.05841	grain per gallon (gr/gal)
gram (g)	0.002205	pound (lb)
	0.03527	ounce (oz)
gram per cubic centimeter (g/cm^3)	62.43	pound per cubic foot (lb/ft^3)
gram per hour (g/h)	0.0005878	ounce per minute (oz/min)
gram per day (g/d)	0.0005878	ounce per day (oz/d)
kilogram (kg)	2.205	pound (lb)
kilogram per hour (kg/hr)	2.205	pound per hour (lb/hr)

Convert degrees Celsius (°C) to degrees Fahrenheit (°F) by using the formula:

$$^\circ F=1.8\ ^\circ C+32$$

Sea level: In this report "sea level" refers to the National Geodetic Vertical Datum of 1929 (NGVD of 1929)—a geodetic datum derived from a general adjustment of the first-order level nets of both the United States and Canada, formerly called "Mean Sea Level of 1929."

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CHAPTER A.—MOVEMENT AND FATE OF CREOSOTE WASTE IN GROUND WATER NEAR AN ABANDONED WOOD-PRESERVING PLANT NEAR PENSACOLA, FLORIDA

ILLUSTRATIONS

CHAPTER A.—MOVEMENT AND FATE OF CREOSOTE WASTE IN GROUND WATER NEAR AN ABANDONED WOOD-PRESERVING PLANT NEAR PENSACOLA, FLORIDA

INTRODUCTION

By Bernard J. Franks[1]

Problems of ground-water contamination from leaking surface impoundments are common in surficial aquifers, and are a subject of increasing concern and attention. A potentially widespread contamination problem involves organic chemicals used in wood-preserving processes. Creosote is the most extensively used industrial preservative in the United States today, with more than 400 wood-preserving plants in the United States collectively using 4.5×10^9 kg (kilograms) of creosote per year (von Rumker and others, 1975). It is estimated that creosote contains more than 200 major individual compounds with differing molecular weights, polarities, and functionalities, along with dispersed solids and products of polymerization (Novotny and others, 1981). Analyses of creosote consist of approximately 85 percent by weight polynuclear aromatic hydrocarbons, 12 percent phenolic compounds, and 3 percent heterocyclic compounds containing nitrogen, sulfur, and oxygen.

Because of the widespread distribution of creosote in the environment, an abandoned wood-treatment plant in Pensacola, Fla., was selected by the U.S. Geological Survey Office of Hazardous Waste Hydrology as one of three national research demonstration areas in order to increase our understanding of hydrologic processes affecting the distributions of contaminants in ground water. The site was selected because of its long, uninterrupted history (1902–81) of discharging wastewaters to unlined surface impoundments, availability of a preliminary data base (Troutman and others, 1984), and the high probability of useful technology transfer from an investigation of the fate of organic compounds associated with wood-preserving wastewaters in the subsurface environment.

Site Description and Hydrogeology

The research site is within the city of Pensacola, Fla., approximately 550 m (meters) north of Pensacola Bay and near the entrance to Bayou Chico, in a moderately dense, commercial-residential area of Pensacola (fig. A–1). The wood-treatment process used throughout the history of the plant consisted of removing as much of the cellular moisture as possible from pine logs and replacing the moisture, under pressure, with either creosote or pentachlorophenol (PCP). Effluent from the treatment process consisted of water, diesel fuel (used as a carrier in the treatment process), creosote, and PCP. Effluent was discharged to shallow unlined surface impoundments with direct hydraulic connection to the underlying sand-and-gravel aquifer. Periodic overtoppings of the embankments around the impoundments have further contaminated the surficial aquifer.

The site is underlain by about 80 m of surficial deposits, constituting the sand-and-gravel aquifer. The aquifer consists of nonhomogeneous fine-to-coarse grained, locally well-sorted fluvial and deltaic sediments. The top of the aquifer is coincident with land surface, with altitudes of less

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[1] U.S. Geological Survey, Tallahassee, Fla.

than 3 m above sea level near the site. The base of the aquifer, 80 m below sea level near the site, is in contact with the top of the Pensacola Clay confining bed. The aquifer has been divided into three permeable zones (Barr and others, 1981): a surficial water-table zone (5–15 m thick near the site), a low-permeability intermediate zone (25 m thick), and a deeper confined zone (40 m thick), which are separated from each other by thin (3–10 m) discontinuous confining clays.

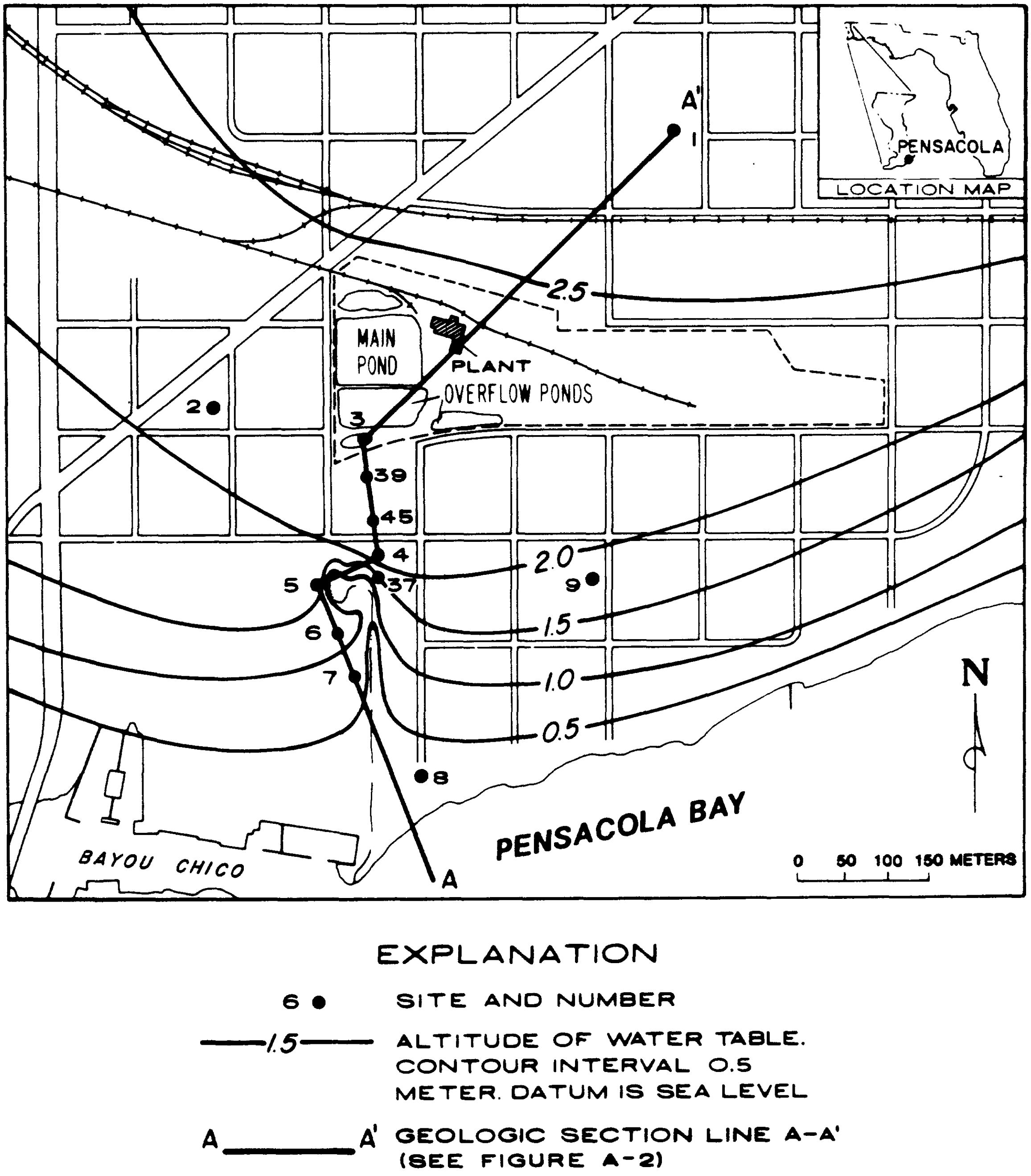

Figure A-1.—Site location and configuration of the water table in the vicinity of the creosote works site.

Ground-water flow is generally southward toward Pensacola Bay, with mean darcy velocities of about 0.2 m/d (meter per day). In the contaminated part of the aquifer, ground-water velocities range from about 0.05 to 1.0 m/d. Recharge, primarily from rainfall, is estimated to contribute about 0.2 m/yr (meter per year) to the aquifer. Discharge is to Pensacola Bay and to a small drainage ditch south of the impoundments. Hydraulic conductivity of the upper two (contaminated) zones ranges between 9 and 20 m/d. Ground-water contamination extends about 600 m south of the contaminant source and, vertically, to about 30 m below land surface encompassing only the upper two zones. A north-south cross section illustrating the vertical extent of contamination is shown in figure A-2.

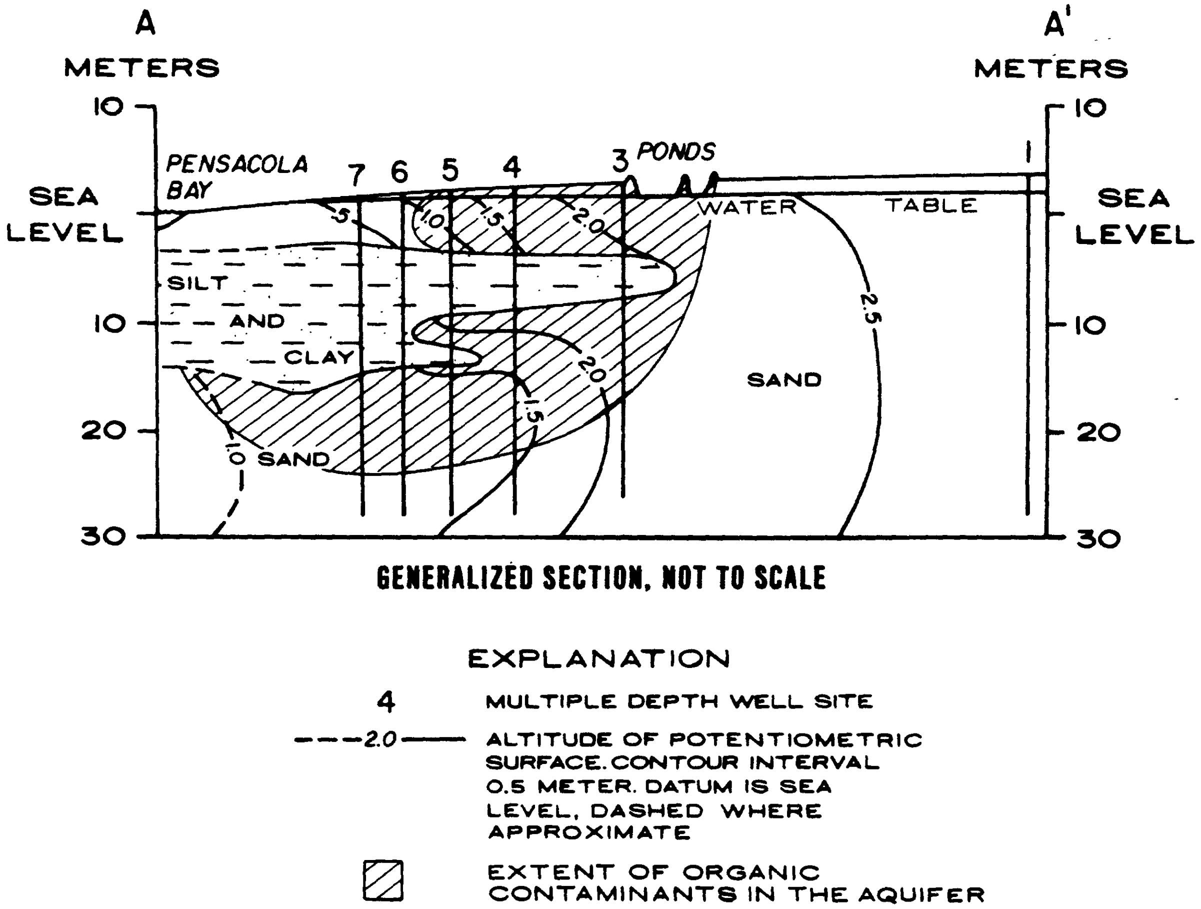

Figure A-2.—Geologic cross section showing lines of equal head and approximate water table, January 1984.

Synopsis of Research Elements

This section summarizes research to date at the Pensacola site, including an introduction to work presented in Chapter A, this report. Preliminary results from the Pensacola site, presented at the Tucson meeting in 1984, are given in Mattraw and Franks (1986). A more integrated understanding of the processes affecting ground-water contamination at the site was presented in 1985 at the Cape Cod meeting (Ragone, in press).

During the first field phase in 1983-84, more than 40 wells were installed at 9 different sites, hydrogeologic data were collected, and innovative techniques of sampling ground water for hazardous organic compounds were developed (Mattraw and Franks, 1986). The water-soluble fraction of creosote was identified and analyzed by gas chromatography-mass spectrometry and high-performance liquid chromatography, and distributions of selected organic contaminants were mapped (Franks and others, 1985; Goerlitz and others, 1985).

Results of this early work highlighted the heterogeneity of the surficial aquifer and the seemingly unpredictable nature of the distribution of organic contaminants in the subsurface. Thus an additional 40 wells at 18 new sites were constructed, in order to better evaluate the subsurface environment underlying the contaminant source. The use of ground-penetrating radar in delineating the shallow stratigraphy (clay/sand) beneath the site was documented by Olhoeft (in press). Further delineation of the depositional environment in the surficial aquifer is presented in Clark and Donoghue (1987). They used grain-size analyses, including selected moment measures, to describe the heterogeneous distribution of sediment properties in the aquifer.

Hydrogeologic data were evaluated using a three-dimensional digital simulation of ground-water flow (Franks, in press). Simplifying assumptions included that hydraulic heads are at steady state, and that the aquifer can be treated as multilayered and isotropic. Sensitivity analysis showed that the simulations were most sensitive to recharge and leakance in the upper part of the aquifer, and relatively insensitive to changes in hydraulic conductivity and to variation of leakance in the deeper part of the aquifer.

A hypothesis relating the occurrence of iron-rich smectite in these sediments to interactions of the native clay minerals with organic contaminants was proposed by Bodine. The occurrence of nontronite (iron smectite) in the contaminated part of the aquifer has been further documented and inferred to be related to interactions between the organic contaminants and the existing clay mineralogy (Bodine, Chapter A, this report).

Dissolved inorganic species have been characterized by Baedecker and Lindsay (1986). They investigated aspects of inorganic geochemistry, including distributions of selected unstable constituents (iron, sulfur, and isotopic carbon species) in the aquifer. Detailed vertical variations in geochemistry of the surficial aquifer, including distributions of dissolved gases (methane and carbon dioxide) and selected inorganic constituents, were further described. Emphasis has recently been placed on understanding the geochemical processes occurring in the upper 10 m of the aquifer. Interactions of the organic contaminant plume with the aquifer are related to the distribution of an anaerobic zone and associated geochemistry within that zone (Cozzarelli and others, Chapter A, this report). They describe ongoing denitrification and methanogenesis in the aquifer, in addition to the recent discovery of high concentrations of metals (including barium, manganese, and nickel) in the aquifer.

One of the previously unanswered questions concerned an evaluation of the reproducibility of organic contaminant concentrations measured in ground water. This is addressed by Franks and others (Chapter A, this report), who evaluate the reproducibility of organic contaminant concentrations in ground water. They report observed variations of up to 30 percent in target organic compound concentrations, even with carefully controlled sampling and analytical techniques. Anomalies in the occurrence and distribution of dissolved organic compounds in the aquifer were initially investigated by Franks and others (1985), who integrated field investigations and sampling with on-site analytical techniques to improve the understanding of contaminant distributions in the aquifer.

The organic concentration data were used, along with results of laboratory experiments, in determining rates of anaerobic degradation of phenolic compounds present in the water-soluble fraction of creosote. Evidence of anaerobic degradation of phenolic compounds, including delineation of a "bioreactor zone" in the surficial aquifer near the contaminant source, was initially presented by Godsy and Goerlitz (1986). They have since documented a three-step sequential degradation process involving nitrogen-containing heterocycles (including quinoline and isoquinoline), phenol, and the isomers of methyl phenol. Intermediate byproducts (acetic acid is the most common) have been identified in laboratory reactors and in field observations (Godsy and others, Chapter A, this report).

Contamination of the nearby estuarine ecosystem in Pensacola Bay has been investigated by Dresler and Elder (in press). They evaluated bioaccumulation of organic contaminants in mollusks, as well as effects of the contaminants on species diversity in the estuarine system.

Ongoing research at the Pensacola site involves continuing work on hydrologic, geochemical, and microbial processes affecting the distribution, movement, and fate of organic contaminants in the aquifer. Results of three-dimensional flow modeling are being used, along with selected inorganic and organic geochemical data, in beginning modeling of solutes in the contaminated aquifer. Organic contaminant chemistry and pathways of microbial degradation are being identified and correlated, both in the laboratory and in field observations. Much of the continuing fieldwork involves documenting and recognizing interactions among the hydrologic processes active in the subsurface environment at the Pensacola site.

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AUTHIGENIC NONTRONITIC SMECTITE ASSOCIATED WITH THE CREOSOTE WASTE PLUME, PENSACOLA, FLORIDA

By Marc W. Bodine, Jr.[1]

Clay minerals in surficial sediments on the western shore of Pensacola Bay, Pensacola, Fla., were investigated in association with a waste plume from an abandoned creosote plant. Downgradient from the plant's waste ponds, the contaminated ground-water plume flows through an unconsolidated sand aquifer system with lenticular sand-to-silty mud interbeds. The ground-water plume, containing abundant organic (phenolitic) pollutants, in places coexists with a second fluid phase of water-immiscible creosote waste. Major chemical characteristics of the aqueous phase in the waste plume include mildly acidic pH (~5 to 6), unusually high concentrations of dissolved iron (with 3 to 10 mg/L (milligrams per liter) common, and up to 40 mg/L in places), low redox (a methane, ammonia, and hydrogen sulfide-(H_2S) bearing system), and moderate concentrations of dissolved silica (5 to 20 mg/L are common).

Kaolinite, dioctahedral aluminous smectites, discrete illite, and chlorite compose the clay-mineral assemblages in the sediments. Kaolinite with lesser amounts of smectite characterize many sand samples; smectite coexisting with less kaolinite dominates most mud units. Illite and chlorite are minor but present in all samples. The kaolinite-rich assemblages appear to be typical Appalachian terrigineous detritus whereas the smectite-rich assemblages are most likely terrigineous clays admixed with characteristic bottom sediments from the Gulf Coast. The sands, particularly those close to contacts with the muds, frequently exhibit grain coatings; outside the waste plume the coatings are virtually monomineralic kaolinite, but within the contaminated area the coatings are smectite-rich and contain authigenic pyrite. Smectite-rich or, less frequently, kaolinite-rich round mud galls up to 3 centimeters in diameter occur in some sands adjacent to the intercalated mud beds. The <2-micrometer insoluble fractions of sediment from within the plume contain 6 to 9 weight percent ferric oxide (Fe_2O_3) whereas those from uncontaminated sediments contain <3 percent Fe_2O_3. X-ray powder diffractometer traces of randomly mounted samples of clay-size fractions from within the plume show pronounced asymmetry of the dioctahedral (060) reflection at ~1.50 Å toward lower Bragg angles with a shoulder or discrete broad second peak occurring at 1.52 Å. These features are interpreted as the occurrence of nontronite (a smectite in which ferric iron instead of aluminum occupies the octahedral sites), or more likely, nontronitic aluminous smectite in the assemblage.

Within the plume, the nontronitic smectite is observed in the pyrite-bearing grain coatings and in the clay galls that are included in the aquifer sands, as well as in the intercalated mud units. The absence of nontronitic clay in stratigraphically equivalent sediments outside the plume suggests its authigenic origin as a result of waste-sediment interaction. Furthermore, the occurrence of the nontronitic clay in the intercalated mud units within the plume strongly suggests some leakage of the waste fluid into the mud units.

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

Recent authigenic nontronite has been reported elsewhere, for example, in the Red Sea geothermal area, in Lake Chad bottom sediments, and in several deep-sea, low-temperature, hydrothermally altered basalts. Nontronite also has been synthesized from gels in laboratory experiments of only several days duration at room temperature under reducing conditions in mildly alkaline (pH=7–9) solutions containing 4 mg/L iron and 20 mg/L silicon dioxide (SiO_2). These chemical constituents are very similar to those produced in the water-sediment system by the creosote waste plume.

EVALUATION OF REPRODUCIBILITY OF ORGANIC CONTAMINANT CONCENTRATIONS IN GROUND WATER CONTAMINATED BY WOOD-PRESERVING WASTES AT PENSACOLA, FLORIDA

By Bernard J. Franks[1], Donald F. Goerlitz[2], and Janet B. Pruitt[1]

Variations in concentrations of target organic compounds measured in ground water from a sand-and-gravel aquifer contaminated by wood-preserving wastes near Pensacola, Fla., may be attributed to sampling techniques and analytical precision and accuracy. The contaminated ground water has been enriched in phenolic compounds (36 percent); heterocyclic compounds, including nitrogen, sulfur, and oxygen heterocycles (29 percent); and organic acids (35 percent) originating from a wood-treatment plant that operated from 1902 to 1981.

In order to evaluate the data variability, sampling and analytical methods were carefully controlled over a 3-year period. Sample collection and preservation techniques and analytical methods were kept uniform. All samples were shipped by overnight delivery and extracted within 48 hours of collection.

Four wells, which provided a representative range of contaminant concentrations, were selected for evaluating the variability resulting from sampling and analysis. All wells were sampled at a flow rate of one liter per minute, immediately after 3 to 30 casing volumes (110–1,100 liters) of water were removed. Concentrations, in milligrams per liter (mg/L), of naphthalene ranged from 0.4 to 11.0; of 3,5-dimethylphenol, from 0.06 to 2.2; and of dibenzofuran, from <0.05 to 0.81. No relation was observed between pumping volume and measured concentrations. There also was no relation between the date of sampling and the measured concentrations, indicating that the aquifer is near steady-state (no time trend) with regard to contaminant concentrations.

Analytical precision and accuracy were evaluated by analyzing replicate ground-water samples, surrogate matrix spikes, and deionized water target and surrogate spikes. The target compound, naphthalene, detected at concentrations above 1 mg/L in all samples, yielded a coefficient of variation (CV) ranging from 0 to 23 percent in 11 sets of replicate samples. Reproducibility of 3,5-dimethylphenol was generally the same as naphthalene, with a CV of 2 to 47 percent in 10 sets of replicates having concentrations ranging from 0.32 to 1.5 mg/L. Eleven replicate sets of dibenzofuran were less reproducible (CV=0–74 percent), as suggested by 1 set of replicates with a CV of 74 percent. The CV for the other 10 replicates ranged from 0 to 14 percent. Reproducibility of two surrogate matrix-spiking compounds, ranging in concentration from 0.04 to 2.0 mg/L, was generally the same as the target compounds, with a CV of 2 to 30 percent. Deionized water spikes containing the three target compounds generally yielded average recoveries of 70 to 80 percent. Surrogate spikes in deionized water had average recoveries of 75 to 85 percent.

Analytical precision was also evaluated by making repeated analyses of the two surrogate compounds in a matrix spike and of a deionized water spike containing the three target compounds. Fifteen analyses of the 2 surrogate matrix spikes and 7 analyses of the deionized water spikes yielded a CV of 2 percent.

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[1] U.S. Geological Survey, Tallahassee, Fla.

[2] U.S. Geological Survey, Menlo Park, Calif.

Observed variations in target organic compounds in ground water are a result of errors in analytical precision and accuracy, and sampling error. Reproducibility varied between 2 and 30 percent, with a mean of about 15 percent. Since sampling techniques were carefully controlled during this investigation, most of the observed variation is assumed to be a result of inherent uncertainties in the analyses of target organic compounds in the subsurface environment.

EFFECTS OF CREOSOTE PRODUCTS ON THE AQUEOUS GEOCHEMISTRY OF UNSTABLE CONSTITUENTS IN A SURFICIAL AQUIFER

By Isabelle M. Cozzarelli[1], Mary Jo Baedecker[1],
and Jessica A. Hopple[1]

A detailed study of the geochemistry of a surficial ground-water system, downgradient of creosote-waste disposal ponds in Pensacola, Fla., was undertaken to examine the effects of organic contaminants on the ground-water chemistry of a quartz-rich sand-and-gravel aquifer. Ground water flows south and discharges into Pensacola Bay 500 m (meters) from the disposal ponds. Previous work at the site (Mattraw and Franks, 1986) has shown that south of the ponds a silt and clay lens separates the leachate into a shallow plume about 2 to 6 m below land surface and a deeper plume about 17 to 35 m below land surface. Land-use changes at the site have resulted in multiple sources of the creosote contaminants. This complicates the investigation of geochemical reactions along flowpaths that include the entire extent of contaminant movement. However, investigations along short transects and in vertical profiles revealed the reactions and processes that control the geochemistry of the ground water. Clusters of wells, screened at approximately 1.5-m intervals, were installed in the shallow plume along two transects, one southwest and another directly south of the disposal ponds, to define the vertical extent of the contaminants and their degradation products.

Water immediately downgradient of the ponds, at 4 to 6 m below land surface, has high dissolved organic carbon (DOC) concentrations (230 mg/L (milligrams per liter)). Organic compounds that are components of creosote (polyaromatic hydrocarbons, phenols, and nitrogen heterocyclics) constitute 67 percent of the DOC in water close to the source. At 350 m downgradient from the source, creosote compounds are not present and a large part of the DOC is from uncharacterized degradation products. Dissolved iron (Fe^{2+}) and hydrogen sulfide (H_2S) initially increase as iron is solubilized under anoxic conditions and then decrease in concentration as they are reprecipitated as iron sulfide (FeS_2) (Baedecker and others, in press). Iron is also incorporated into clays which are present in the aquifer as lenses and coatings on sand grains (Bodine, Chapter A, this report). Methane (CH_4) concentrations decrease from 13 mg/L near the source to 0.1 mg/L near the bay. Production of CH_4 from the degradation of organic matter results in isotope fractionation and the accumulation of isotopically heavy total inorganic carbon (TIC). TIC near the source has heavy $\delta^{13}C$ values of -7 $^{o}/_{oo}$ (per mil) to -9 $^{o}/_{oo}$ (relative to the Peedee belemnite (PDB) standard) compared to background values of -19 $^{o}/_{oo}$ to -21 $^{o}/_{oo}$, and CH_4 has light $\delta^{13}C$ values of -58 $^{o}/_{oo}$ to -60 $^{o}/_{oo}$. The amount of isotopic fractionation decreases rapidly downgradient which indicates that mixing with uncontaminated ground water is an important attenuation process.

Although the creosote compounds are present 4 to 6 m below land surface, the effects of the contamination on the chemistry of the aquifer extend up toward the water table (1.5 m below land surface). Along the southwest transect, near the source, oxygen (O_2) is depleted and nitrate (NO_3^-) is reduced 1 m below the water table. Sulfate (SO_4^{2-}) concentrations show a maximum (19 mg/L) at 3 m below land surface and then decreases sharply with depth to 0.4 mg/L at 6 m. Over the same depth range, the

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[1] U.S. Geological Survey, Reston, Va.

concentration of H_2S increases to 4 mg/L as a result of microbial reduction of SO_4^{2-}. Other constituents show marked increases in concentrations from the water table to 6 m. DOC concentrations increase from 2.8 mg/L to 121 mg/L, CH_4 concentrations increase from 0.01 to 14 mg/L, and TIC concentrations increase from 3 to 23 mg/L. The $\delta^{13}C$ values of TIC, which are light (-25 $^{o}/_{oo}$) near the water table, are heavy (-9 $^{o}/_{oo}$) at 6 m below land surface. Further downgradient (325 m southwest of the ponds), the vertical profile shows more gradual changes with depth for these dissolved constituents. In addition, the $\delta^{13}C$ values of TIC show little change with depth (-22 $^{o}/_{oo}$ at 3 m below land surface to -20 $^{o}/_{oo}$ at 6 m below land surface). Mixing of the ground water as it moves away from the source toward Pensacola Bay appears to dilute concentrations of CH_4, DOC, and TIC and minimize the changes observed with depth.

At another location, downgradient of the ponds (150 m south), ground water is anoxic at the water table and has high concentrations of DOC, H_2S, and CH_4. These conditions at shallow depths may reflect the influence of overland flow of contaminants that occurred during overtopping of nearby disposal ponds. The heavy $\delta^{13}C$ values of TIC (-3.9 $^{o}/_{oo}$ and -3.5 $^{o}/_{oo}$) suggest that a substantial amount of the CH_4 and carbon dioxide (CO_2) was generated from microbial processes. In addition, the major inorganic ions and several metals including barium, molybdenum, manganese, nickel, and strontium, are as much as two orders of magnitude above background concentrations and show marked changes with depth. The maximum metal concentrations are found in the zones of high iron, CO_2, and CH_4 concentrations.

Most organic contaminants associated with creosote are attenuated or completely degraded in the shallow plume 270 m downgradient from the source. However, products from the degradation of these compounds alter the aqueous geochemistry of the aquifer over a larger area in both vertical and horizontal directions. The extent to which these alterations occur is dependent on the absence or presence of clay in the aquifer, rates of biodegradation of the contaminants, and mixing of the ground water.

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ANAEROBIC BIODEGRADATION OF CREOSOTE CONTAMINANTS IN NATURAL AND SIMULATED GROUND-WATER ECOSYSTEMS

By Edward M. Godsy[1], Donald F. Goerlitz[1], and Dunja Grbić-Galić[2]

Creosote contaminants in a surficial sand aquifer result in two distinct phases in the subsurface: a denser-than-water hydrocarbon phase that moves vertically downward somewhat perpendicular to the ground-water flow, and an organic-rich aqueous phase. The higher density phase is assumed immobile in the aquifer beneath the site and available as a contaminant source. The aqueous phase is enriched in organic acids (35 percent), phenolic compounds (36 percent), single and double ring aromatic compounds (4 percent), and single and double ring nitrogen, sulfur, and oxygen containing aromatic compounds (25 percent). These dissolved contaminants are subject to physical, chemical, and biological processes that will tend to retard their movement relative to the ground water.

The overall research objectives of this study were: (1) to establish laboratory microcosms simulating the subsurface environment in order to determine which compounds in the aqueous phase were anaerobically biodegradable, (2) to determine the nature of the microbial population in the aquifer sediments, and (3) to compare the results of laboratory transformations to field observations of temporal and spatial changes in subsurface distribution of major compounds during downgradient movement from site 3 to site 37 (*see* fig. A-1).

The existence of microbes in the subsurface has only recently come to light. Several studies have clearly demonstrated the existence of active microbes in these environments (for example, Harvey and others, 1984). Determination of the physiological groups in the resident population often helps in determining the ultimate fate of the contaminants during downgradient movement in the aquifer and was instrumental in determining the fate of coal-tar derivatives at a contaminated ground-water site at St. Louis Park, Minn. (Ehrlich and others, 1983). Microbiological analysis of the aquifer material and the corresponding pore water at the six sites has revealed that a small, but apparently active population of bacteria resides in the subsurface and that at least 90 percent of this population is attached to the aquifer material. These analyses revealed that the only apparent difference between the contaminated sites and the uncontaminated site was a 10- to 100-fold increase in the number of methanogenic bacteria in the contaminated area.

Various pathways have been proposed for the anaerobic degradation of aromatic compounds depending on the nature of the substrate, but they are all similar in the major steps involved: (1) the removal of substituent side groups by reduction, demethylation (Szewzyk and others, 1985; Young and Rivera, 1985) demethoxylation, dehydroxylation, and decarboxylation (Grbić-Galić and Young, 1985); (2) incorporation of oxygen from water into the ring structure of compounds that do not already have oxygen incorporated (Vogel and Grbić-Galić, 1986; Berry and others, 1987); (3) hydrogenation of the aromatic structure with the formation of an alicyclic intermediate; (4) fission of the alicyclic compounds to straight chain acids; (5) conversion of these acids to acetate, hydrogen, and carbon dioxide; and (6) under methanogenic conditions, conversion of these end products to methane.

[1] U.S. Geological Survey, Menlo Park, Calif.

[2] Stanford University, Stanford, Calif.

This study indicates that, along with the phenolic compounds and organic acids previously reported to be anaerobically biodegradable (Godsy and Goerlitz, 1986), the nitrogen containing compounds (quinoline, isoquinoline, 2(1H)-quinolinone and 1(2H)-isoquinolinone) are also anaerobically biodegradable to methane and carbon dioxide. It was observed that a three-step sequential degradation of these compounds occurred in which the compounds in group one were degraded before phenol and those in group three were degraded after phenol:

1. Quinoline, isoquinoline, benzoic acid, and three through six carbon volatile fatty acids;
2. Phenol; and
3. 2-, 3-, and 4-methylphenol, 2(1H)-quinolinone, and 1(2H)-isoquinolinone.

Acetic acid is the major intermediate compound in the conversion of the biodegradable compounds in the aqueous fraction. This is very similar to conventional anaerobic domestic sewage sludge digestors where acetic acid is the major intermediate compound in the conversion of complex substrates to methane and carbon dioxide. The volatile fatty acids are rapidly converted to acetate in the digestor along with those degradable compounds in step one. An increase in acetate is also observed during each of the other steps of the sequential degradation.

Inorganic analyses of water samples from the contaminated area clearly demonstrate that anoxic conditions prevail. The contaminated ground water is devoid of dissolved oxygen, is approximately 60 to 70 percent saturated with respect to methane, and contains a relatively high concentration of hydrogen sulfide (Cozzarelli and others, Chapter A, this report). Sufficient nitrogen and phosphorus are present to allow for microbial degradation of susceptible organic compounds. The concentrations of phenol, 2-, 3-, and 4-methylphenol, quinoline, isoquinoline, 2(1H)-quinolinone, and 1(2H)-isoquinolinone decrease disproportionately downgradient when compared to the conservative tracer 3,5-dimethylphenol.

The ground-water velocity in the area of the plant has been determined to range from 0.1 to 1.0 m/d (meters per day). Flow velocities at the 6.1-m (meters) sampling depth have been determined to be on the order of 1 m/d. This value allows for easy comparison of laboratory and field data; residence time in the aquifer approximately equals the downgradient distance traveled. The approximate downgradient distance of the contaminated sites from the source ponds are as follows: site 3, 6 m; site 39, 53 m; site 45, 99 m; site 4, 122 m; and site 37, 150 m. Comparison of the composition of the major compounds in the aqueous fraction of the ground-water samples to the digestor composition after a comparable time of residence facilitates recognition of the disappearance pattern observed in the ground-water samples. During the first 50 days of residence in the digestors, or travel from site 3 to site 39, the 3 through 6 carbon volatile fatty acids are rapidly converted to acetic acid and ultimately to methane and carbon dioxide. Benzoic acid, quinoline, and isoquinoline are also biodegraded. Phenol degradation occurs between days 50 and 99 in the digestors and phenol also disappears from the ground water during transit from site 39 to site 40. After 100 days in the digestor, 2-, 3-, and 4-methylphenol, 2(1H)-quinolinone, and 1(2H)-isoquinolinone are biodegraded and are removed from the system after about 200 days. A similar pattern of disappearance is observed during travel from site 40 to site 4 for 2-, 3-, and 4-methylphenol; however, the degradation of 1(2H)-isoquinolinone is delayed somewhat compared to the digestors.

Integration of both laboratory results and field observations helps in determining the ultimate fate of the subsurface contaminants. Results demonstrate that the disproportionate decrease of selected organic compounds observed during downgradient movement in the aquifer can be attributed to microbial degradation of these compounds. The anoxic conditions in the contaminated area, high concentrations of dissolved methane, and the increased numbers of methanogenic bacteria suggest that methanogenic fermentation was the predominant microbiological process. This observation was confirmed in the laboratory digestors.

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CHAPTER B.—FATE AND TRANSPORT OF CONTAMINANTS IN SEWAGE-CONTAMINATED GROUND WATER ON CAPE COD, MASSACHUSETTS

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CHAPTER B.—FATE AND TRANSPORT OF CONTAMINANTS IN SEWAGE-CONTAMINATED GROUND WATER ON CAPE COD, MASSACHUSETTS

INTRODUCTION

By Denis R. LeBlanc[1]

In 1983, a sewage plume on Cape Cod, Mass., was among three sites chosen by the U.S. Geological Survey's Toxic Waste—Ground-Water Contamination Program for studying contaminant transport and attenuation in aquifers. The site was chosen because of its 45-year history, its relatively simple hydrogeologic setting, and its similarity to many contamination sites nationwide.

The sewage plume is located on western Cape Cod near Falmouth, Mass. (fig. B-1). Since 1936, infiltration beds at the site have been used to dispose of sewage that has undergone secondary treatment. Except for a brief period of increased flow during World War II, flow from the plant has remained relatively constant and presently averages 1.1 million liters per day. The effluent contains about 170 mg/L (milligrams per liter) dissolved solids, which is four times greater than the dissolved-solids content of the native ground water. Major contaminants in the effluent presently include chloride, boron, sodium, ammonium- and nitrate-nitrogen, and detergents, and probably included volatile-organic compounds between about 1950 and the mid-1970's.

The treated sewage recharges a glacial-outwash aquifer that is composed of 30 to 40 m (meters) of stratified sand and gravel and is underlain by silty sand and till. The aquifer also receives about 50 centimeters per year areal recharge from precipitation. Estimated properties of the outwash include a hydraulic conductivity of 0.07 to 0.13 centimeters per second and an effective porosity of 0.35 to 0.40. Ground water is unconfined and moves southward toward Nantucket Sound at a velocity of 0.3 to 0.4 m/d (meters per day), where it discharges to coastal wetlands, streams, and the ocean.

INITIAL STUDY OF THE SEWAGE PLUME

The sewage plume was first described by the U.S. Geological Survey in a study done in cooperation with the Massachusetts Division of Water Pollution Control (LeBlanc, 1984a). In 1979, the plume was 20 to 25 m thick, 750 to 1,100 m wide, and more than 3,500 m long. About 6 to 15 m of uncontaminated ground water from areal recharge overlay the plume.

This initial study showed that contaminants in the plume were transported with the ground water, but were also altered by chemical reactions and had entered the aquifer at different rates. Chloride, sodium, and boron seemed to be transported conservatively and had spread from the source mainly by advection and dispersion, while phosphorus was apparently retarded by sorption and had moved only 600 m from the infiltration beds. Ammonium-nitrogen seemed to be transformed to nitrate by microbially mediated nitrification in a zone located about 2,100 m from the beds. Detergent concentrations were elevated in a zone from 900 to 3,000 m from the infiltration beds because nonbiodegradable detergents were used between about 1950 and 1964.

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

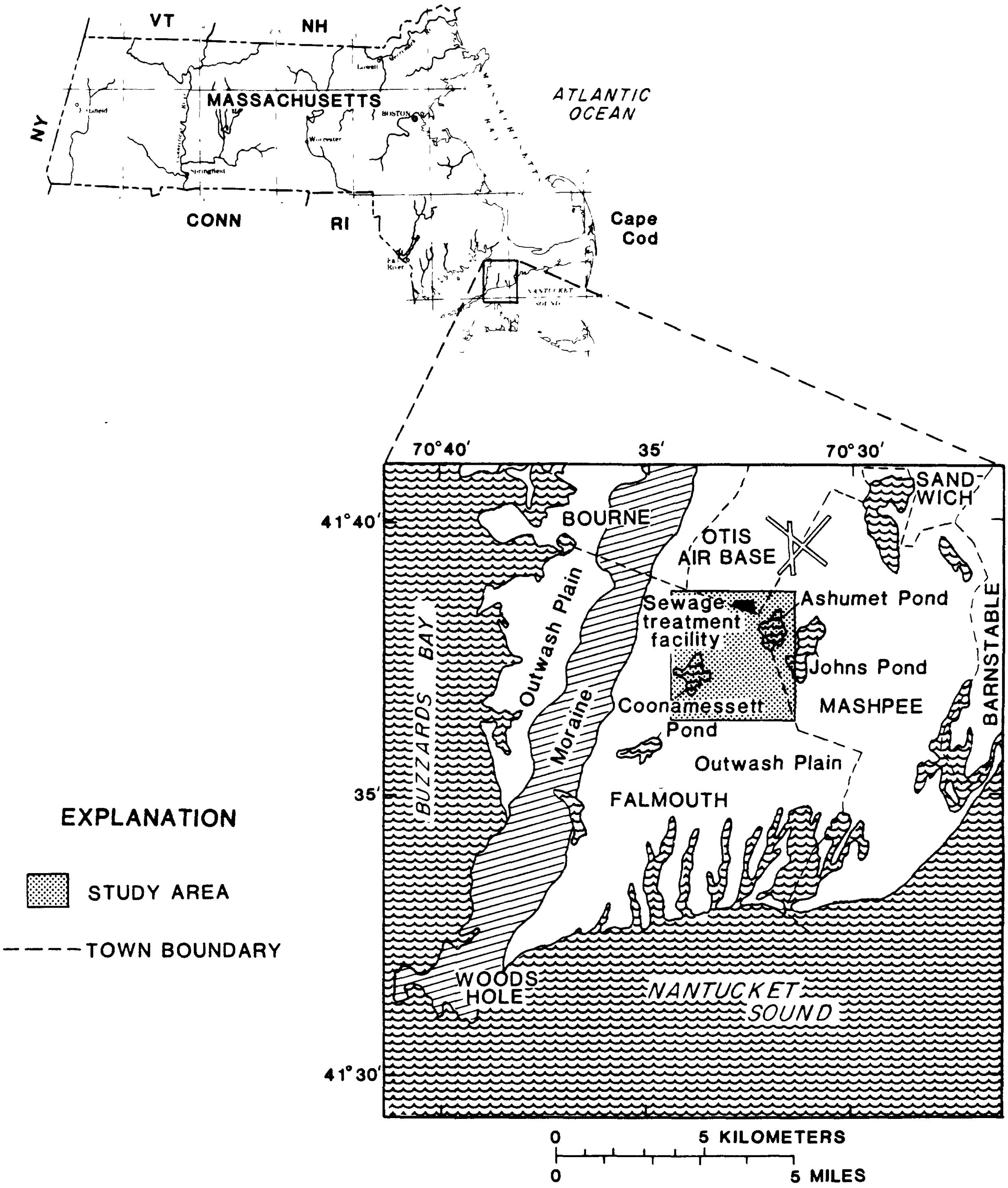

Figure B-1.—Location of Cape Cod, Massachusetts, study site.

FIRST PHASE OF RESEARCH

In the first phase of research sponsored by the Toxic Waste—Ground-Water Contamination Program, which is described in LeBlanc (1984b) and Ragone (in press), hypotheses concerning transport of contaminants were proposed and testing of these hypotheses began. During this phase, transport of boron and detergents was simulated with a two-dimensional model, and wells were drilled and sampled for major inorganic contaminants, organic compounds, and indigenous bacteria. Examples of these results are included here.

Ground-water velocities were measured in the first phase of research because transport in the plume is predominantly by advection. In the two-dimensional model, the best match between the observed and simulated plumes was obtained with a velocity of 0.3 m/d, which is lower than velocities of about 0.4 m/d measured in tracer tests and estimated from aquifer properties at a pumping-test site. Travel distances in the plume over 50 years, based on the two values, differ by 1,800 m, or about 50 percent of the apparent length of the plume in 1979. These different values may be the result of variations in hydraulic conductivity in the stratified sediments. In the tracer tests, travel times differed by factors of two or three in zones only 0.6 m apart.

Bacterial populations were measured in the plume for the first time in 1983, and were as high as 2 million per milliliter near the infiltration beds, but at 1,000 m from the beds had decreased to about 250,000 per milliliter. These numbers seemed to correlate with availability of degradable organic compounds; concentrations of dissolved organic carbon decreased from 12 mg/L to less than 2 mg/L over the same distance. The decrease in bacterial numbers with distance, particularly bacteria smaller than 0.4 micrometer in diameter, also suggested that transport of bacteria is occurring. Other studies have shown that large bacteria are transported through porous media more readily than small bacteria.

Measurement of rates of microbial activity in the plume was also part of the first phase of research. Assays of microbial activity were run on both water and sediments because more than 90 percent of bacteria were found attached to silt- and clay-sized particles. Efforts focused on nitrogen transformations, and rates of denitrification were greatest in water and sediment samples collected in a 1-m to 2-m thick zone near the top of the plume.

Volatile-organic compounds were found in the plume for the first time in 1983. Concentrations of these toxic compounds were greater than 50 micrograms per liter in a zone from 500 to 2,600 m from the infiltration beds, which suggested that they are mobile and not readily degraded in the sandy aquifer. Trichloroethene, tetrachloroethene, and dichlorobenzene had traveled farther than nonylphenol in accord with estimated retardation rates based on hydrophobicity of the compounds. However, the relative importance of changes in the concentration of these compounds in the sewage, their retardation by sorption on the sediments, and their biodegradation was not known.

CURRENT RESEARCH

Observed distributions of contaminants and bacteria were used in the first phase of research to infer major processes that affect transport and attenuation in the plume. Two factors limit adequate testing of these hypotheses. First, the history of chemical quality of the treated sewage is largely unknown. Second, methods to measure rates of dispersion and reactions in the aquifer are inadequate. Unknown source history and inadequate sampling methods are problems that face investigators at most toxic-waste sites. Therefore, current research at the Cape Cod site, which is described in this chapter, has focused on developing and using field experiments and sampling methods to better understand transport processes.

The first four abstracts in this chapter describe the initial results of a natural-gradient tracer test which is a major part of current research. The test was run to measure dispersion and to determine geochemical controls on nonconservative transport in a heterogenous aquifer. Bromide, a conservative tracer, was monitored with an array of 9,600 sampling points as it moved 290 m through the aquifer. Statistical analysis of bromide concentrations has shown that dispersivity is about 0.9 m in the direction of flow and is very small transverse to flow. Two nonconservative tracers, lithium and molybdenum, are moving at a rate about 0.7 times the average velocity of the bromide. This degree of retardation is consistent with estimates of retardation from laboratory tests of the sediment from the site. Dispersion of the tracers is related to variations in hydraulic conductivity. Hydraulic conductivities are being measured at close intervals in about 40 continuous cores using a constant-head permeameter and compared to values determined by grain-size analyses and piezometer tests. These values and the tracer-test results will be used to test stochastic theories relating dispersion to variations in hydraulic conductivity.

The next three abstracts describe a series of tests that are being used to measure microbial activity and transport in the aquifer. To locate areas where denitrification is suspected of occurring, assays are being run on water and sediment samples collected with multilevel sampling devices and a piston core barrel that retains interstitial ground water. Detailed sampling using these methods at one site 300 m from the infiltration beds has shown that microbial activity, chemical indicators of reactions, and bacterial numbers can change greatly over vertical intervals as small as 1 to 2 m. A method for using tracers to measure microbial activity directly in the aquifer was tested using methane and Freon[2] as tracers. These dissolved gases were transported without retardation, but concentrations of methane decreased because of apparent biodegradation. Two tracer tests showed that transport of bacteria may be affected by bacterial size and electrical charge on the surfaces of the bacteria. In one test, the bacteria moved conservatively with chloride through about 7 m of the aquifer under a natural hydraulic gradient.

The last four abstracts describe one-dimensional models, geochemical analyses of sediments, and tracer tests that are being used to determine the processes that retard movement of organic compounds and ammonium-nitrogen in the plume. The one-dimensional models are being used to determine if ground-water velocities and reaction rates determined by field and laboratory experiments can be used to explain the observed distributions of contaminants. Initial model analyses yielded a ground-water velocity of 0.3 m/d, which agrees with the earlier two-dimensional model. The analyses also showed that the ammonium-nitrogen concentrations are not explained by estimated rates of retardation and nitrification. To improve these estimates, a tracer test was run with ammonium- and nitrate-nitrogen as tracers. The test showed that ammonium is retarded by ion exchange relative to a conservative tracer, releasing cations such as calcium, magnesium, and potassium into solution that are normally sorbed on the sediments. Preliminary

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

examination of sediment mineralogy and grain coatings showed that, although the organic-carbon content of the sediments is low (about 0.015 percent), hydrophobic organic compounds may be retarded in the sandy sediments.

Plans have been made to test the experimental results described in this chapter using various computer models of solute transport in the sewage plume and in contaminant plumes in similar hydrogeologic environments. Additional reports on research at the Cape Cod site are listed in the bibliography at the end of this report.

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NATURAL-GRADIENT TRACER TEST IN SAND AND GRAVEL: OBJECTIVE, APPROACH, AND OVERVIEW OF TRACER MOVEMENT

By Denis R. LeBlanc[1], Stephen P. Garabedian[1], Warren W. Wood[2],
Kathryn M. Hess[1], and Richard D. Quadri[1]

A natural-gradient tracer test is being conducted at a site on Cape Cod, Mass., to study dispersive transport and chemical processes in a heterogeneous aquifer. In the classical advection-dispersion equation, dispersive flux of solutes is proportional to the concentration gradient, ground-water velocity, and dispersivity, which is assumed to be a constant property of the aquifer. This relation between dispersive flux and concentration gradient is analogous to Fick's second law (Freeze and Cherry, 1979, p. 104).

Several field experiments have suggested, however, that dispersive flux may not follow a Fickian relation and that dispersivity may depend on the distance traveled by the solutes. Non-Fickian dispersion has been observed during early times in several natural-gradient tracer tests (Sudicky and others, 1983; Mackay and others, 1986). Values of dispersivity measured by tracer experiments in the field and those estimated during modeling of contaminant plumes seem to depend on the distance traveled by the solutes and are much larger than values reported for column experiments (Anderson, 1979; Gelhar and others, 1985). Gelhar and Axness (1983) and others have shown theoretically that this dependence on scale and the large values of field dispersivity are caused by spatial heterogeneity of aquifer properties, particularly hydraulic conductivity.

The natural-gradient tracer test on Cape Cod, Mass., was designed to test the relationship between field-scale dispersion and aquifer heterogeneity developed by Gelhar and Axness (1983). In this experiment, dispersion of a conservative and several nonconservative solutes is measured in the field during a tracer test. Next, heterogeneity of the aquifer is determined by measuring the spatial variability of aquifer properties, especially hydraulic conductivity, at the tracer-test site. Dispersivity is then predicted using the methods of Gelhar and Axness (1983), and the predicted and measured values are compared to test the validity of the relationships between heterogeneity and dispersivity.

The tracer test is being conducted in an abandoned gravel pit near the Otis Air Force Base. The aquifer at the test site is composed of stratified sand and gravel outwash of glacial origin more than 30 m (meters) thick. The hydraulic conductivity is about 0.13 cm/s (centimeter per second) and effective porosity is about 0.38. The water table is 3 to 7 m below land surface and slopes southward at a gradient of about 0.0014. Average ground-water velocity, estimated by Darcy's law, is 0.4 m/d (meter per day).

The tracer test began on July 18, 1985, with the injection of a pulse of tracers into the aquifer. The injected solution contained four tracers dissolved in 7.6 m^3 (cubic meters) of water: 4,900 g (grams) of bromide as lithium bromide, 380 g of fluoride as lithium fluoride, and 610 g of molybdenum as lithium molybdate (total lithium of 595 g). The bromide was expected to move conservatively, but the lithium, fluoride, and molybdenum were expected to be retarded by sorption. Equal amounts of tracer solution

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

[2] U.S. Geological Survey, Reston, Va.

were injected at a constant rate in three wells over 16 hours. The wells are spaced 0.9 m apart and have 1.2 m-long screens set about 1 m below the water table.

The tracer cloud has been monitored for 17 months as it moves with the ground water. Water samples are collected about once a month from an array of multilevel sampling devices. Each device includes 15 sampling ports spaced 25 to 76 cm (centimeters) apart vertically to provide vertical profiles of tracer concentrations. The 640 sampling devices are arranged in 71 rows extending about 300 m downgradient from the injection wells. As of December 1986, 16 sampling rounds had been completed. During each round, as many as 10,000 water samples were collected from 40 to 300 sampling devices to obtain a three-dimensional "snapshot" of the tracer distributions.

The observed rate and direction of movement of the conservative tracer, bromide, match that predicted from the water-table gradient and aquifer properties. The rate of movement of the cloud between July 19, 1985, and October 9, 1986, was about 0.4 m/d, which matches the velocity predicted by Darcy's law from estimated hydraulic parameters. The cloud moved along a southward trajectory that generally followed the path predicted from the slope of the water table.

The bromide cloud moved vertically downward about 3 m during the first 200 days of transport. This vertical movement was probably caused by the difference in density between the injected solution and the native ground water as well as by the accretion of recharge at the water table. The initial concentration of dissolved solids in the tracer solution was about 890 mg/L (milligrams per liter); dissolved solids concentration of the native ground water ranged from 40 to 150 mg/L. According to Hubbert's (1953) method of calculating fluid potential, this density contrast is sufficient to cause sinking of the tracer cloud during the early part of the test. When bromide concentrations declined from more than 500 mg/L to 62 mg/L, the downward movement of the tracer cloud stopped. Part of the vertical movement of the tracer cloud may also be due to vertical flow caused by areal recharge. During the first 200 days of the test, total precipitation was 81 cm and the water table rose about 0.2 m.

The bromide cloud spread significantly in the longitudinal direction during transport, but spread much less transverse to flow. At 460 days after injection, the cloud was about 100 m long and only 14 m wide, and peak bromide concentrations had decreased from more than 500 mg/L to 40 mg/L. After the initial spread during injection, the bromide cloud spread vertically only slightly and remained about 4 to 6 m thick as it moved downgradient.

The tracer cloud is asymmetrical along its longitudinal axis and exhibits two zones of elevated bromide concentrations. One zone of high concentration is near the water table and ahead of a second, lower zone. The zones were observed in the first view of the cloud taken 13 days after injection and have persisted in all subsequent views. The two zones were probably formed during injection because of variations in hydraulic conductivity near the injection wells and remain because vertical mixing is small. The leading edge of the bromide cloud occurs near the water table and moved forward as much as 1 m/d during the early part of the test; the average velocity of the leading edge over 460 days was about 0.6 m/d. The higher velocity near the water table may reflect a zone of higher hydraulic conductivity that has caused movement of the leading edge well ahead of the main bromide cloud.

The lithium cloud followed a similar trajectory to the bromide cloud. However, its average rate of movement of about 0.3 m/d was 0.1 m/d slower than the bromide cloud. Laboratory tests of sediments from the test site give a distribution coefficient (K_d) for lithium of about 0.15 mL/g (milliliter per gram). The retardation coefficient is 1.6, assuming that the isotherm is linear and retardation is caused by equilibrium sorption. This retardation value is consistent with observed retardation of the lithium cloud. The movement of molybdenum is discussed by Stollenwerk and Grove (Chapter B, this report).

Data from the tracer test are being used to calculate dispersivity values (Garabedian and others, Chapter B, this report) which will be compared to values calculated from stochastic analysis of hydraulic-conductivity variations (Hess and others, Chapter B, this report). The data are also being used to test methods to design sampling arrays (C. Voss and D. Knopman, U.S. Geological Survey, written commun., 1987) and to predict the movement and fate of nonconservative species from field and laboratory measurements (Stollenwerk and Grove, Chapter B, this report).

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NATURAL-GRADIENT TRACER TEST IN SAND AND GRAVEL: RESULTS OF SPATIAL MOMENTS ANALYSIS

By Stephen P. Garabedian[1], Denis R. LeBlanc[1], Kathryn M. Hess[1], and Richard D. Quadri[1]

A large-scale natural-gradient tracer test has been in progress for more than 17 months as part of the U.S. Geological Survey's toxic waste study at Otis Air Force Base on Cape Cod, Mass. (LeBlanc and others, and Hess and others, Chapter B, this report). This tracer test is designed to examine chemical and physical processes, particularly dispersion, that affect solutes during transport in sand-and-gravel aquifers. Dispersive flux, the spread of solutes around a mean position, in aquifers has often been assumed to equal the concentration gradient multiplied by the solute velocity and dispersivity, which is assumed to be a constant property of a porous medium. This relationship is analogous to Fick's law and is often referred to as Fickian dispersion. However, previous natural-gradient tracer tests in aquifers (Sudicky and others, 1983; Freyberg, 1986; Mackay and others, 1986) have shown that a significant period of non-Fickian dispersion, in which the dispersivity increases, can occur during the early stage of these tests. Anderson (1979) has noted several examples of solute transport in which field-measured dispersivity values were many times larger than those measured in laboratory column experiments and concluded that dispersivity is scale dependent.

Recent theoretical studies (Dagan, 1982; Gelhar and Axness, 1983) have shown that spatial variations of hydraulic conductivity greatly increase the dispersion of solutes in aquifers. These studies support the experimental observation that dispersivity is scale dependent, and that there is a significant period in which the spreading of solutes cannot be described using the Fickian analogy. These studies also indicate that an asymptotic value of dispersivity should be reached after some time.

The objective of dispersion studies at the Cape Cod site is to test these theories by measuring the rates that solutes spread in glacial outwash and relating these rates to statistical characteristics of the hydraulic conductivity distribution (Hess and others, Chapter B, this report).

In addition to tracer test results reported by LeBlanc and others (Chapter B, this report), data from the Cape Cod tracer test have been analyzed by calculating the spatial moments of the conservative solute, bromide, at various times during the experiment. The spatial moments include total mass (zeroth moment), mean position (first moment), and variance (second moment) of the bromide cloud. It can be shown that if dispersion is Fickian and solute velocity constant, dispersivity is equal to one-half the change in variance with respect to travel distance.

Moments for each sampling round were calculated using a numerical integration scheme to solve the general moments equation:

$$M_{ijk} = \iiint_{-\infty}^{\infty} n\, c\, x^i\, y^j\, z^k\, dx\, dy\, dz \qquad (1)$$

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

where:

n = porosity,
c = concentration (mass/volume),
x,y,z = coordinate directions (length).

The spatial moments were calculated using equation (1),

$$\text{total mass} = M_{000},$$

$$\text{mean position } (\bar{x},\bar{y},\bar{z}) = \frac{M_{100}}{M_{000}}, \frac{M_{010}}{M_{000}}, \frac{M_{001}}{M_{000}}$$

$$\text{variance terms} = \frac{M_{200}}{M_{000}} - \bar{x}^2, \quad \frac{M_{020}}{M_{000}} - \bar{y}^2, \quad \frac{M_{002}}{M_{000}} - \bar{z}^2,$$

$$\frac{M_{110}}{M_{000}} - \overline{xy}, \quad \frac{M_{101}}{M_{000}} - \overline{xz}, \quad \frac{M_{011}}{M_{000}} - \overline{yz}.$$

The numerical approach used to solve equation (1) is a trapezoidal integration over the vertical for each set of multilevel concentrations and a triangular integration using linear interpolation over the horizontal. Input for the computer program used to calculate the moments included sampler concentrations and positions and an index list relating horizontal locations to form triangles. In addition to moment calculations, values of the principal axes and rotation angles of the variance tensor were calculated using an eigenvalue solution.

Calculated total mass for each sampling round varied between 86 to 105 percent of the total injected mass. The differences between the calculated total mass and the injected mass are likely due to errors made estimating porosity, analyzing bromide, and interpolating the data. The lack of any trend in the calculated mass with travel distance confirms conservative transport of the bromide ion.

The horizontal displacement of the center of mass followed a nearly constant velocity of 0.43 m/d (meter per day). The center of mass moved downward only during the first 200 days. This pattern of vertical movement indicates that vertical flow of the solute cloud depends on density contrasts early in the test before the solute cloud has mixed with native ground water.

A nonlinear trend in longitudinal variance with travel distance was observed during the first 40 m (meters) of distance traveled, and the dispersion process was non-Fickian in the early part of the test. However, the change in longitudinal variance with travel distance followed a linear trend after the solute cloud had traveled 40 m and it is apparent that a Fickian limit had been reached. The longitudinal dispersivity, given by one-half the slope of the least squares regression line, is about 0.96 m. The strong correlation (0.99) indicates that the change in variance with travel distance is linear, and thus dispersion is Fickian. Some scatter is observed around the linear trend at later times. This scatter is due to errors in the chemical analyses at low concentrations, primarily in the leading and trailing edges of the cloud, which significantly affect the second moment calculations. The change in transverse horizontal and vertical variance with travel distance also show significant scatter around linear trends. This scatter is probably due to sampling density relative to the size of the solute cloud. Transverse horizontal dispersivity is about 1.8 cm (centimeters) and transverse vertical dispersivity is about 0.15 cm.

Major conclusions from moments analysis of the Cape Cod tracer test results are: (1) longitudinal mixing was the dominant dispersion process, which reached a Fickian limit after 40 m; (2) transverse horizontal and vertical dispersion were relatively small; and (3) the horizontal displacement of the solute cloud was accurately predicted using estimates of hydraulic conductivity, porosity, and measured hydraulic gradient. Results of tracer tests at a site in Ontario, Canada (Freyberg, 1986; Mackay and others, 1986) and the Cape Cod site show uniform velocity of the conservative solute, similiar values of longitudinal dispersivity (0.43 m for the Canadian site, 0.96 m for Cape Cod), and small values of transverse dispersivity. Results of the Cape Cod tracer test show that solute concentrations are highly variable and difficult to predict on a small scale but that average characteristics (that is, moments) can be predicted. It is likely that this general result will be valid for other types of aquifers where the material's heterogeneity is regular.

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NATURAL-GRADIENT TRACER TEST IN SAND AND GRAVEL: NONCONSERVATIVE TRANSPORT OF MOLYBDENUM

By Kenneth G. Stollenwerk[1] and David B. Grove[1]

INTRODUCTION

Modeling the transport of a particular solute in ground water requires knowledge of the interactions between the solute and the geologic media. Data that define this knowledge are often obtained by reacting samples of ground water containing the solute with the solid matrix in a laboratory under controlled experimental conditions. Reaction parameters (equilibrium sorption coefficients, rate constants, and such) obtained from these laboratory experiments are then used in solute transport models to predict the behavior of the solute in natural systems. An important question concerns the accuracy of laboratory experiments in approximating the actual behavior of a solute in an aquifer.

There are three primary goals of this research: (a) to identify the type of data that need to be collected in order to adequately model the transport of a nonconservative solute in ground water, (b) to study the geochemistry of the system and identify mechanisms responsible for adsorption and desorption of the solute, and (c) to model the transport and reaction of the solute in laboratory and field environments. Preliminary results relating to b and c are presented here.

Preliminary laboratory experiments indicated that molybdate (MoO_4^{2-}) would react with Cape Cod alluvium, thus MoO_4^{2-} was introduced with other constituents in the initial injection pulse of the natural-gradient tracer test at Cape Cod. Knowledge gained from studying the reactions of MoO_4^{2-} is likely to apply to other more toxic oxyanions such as chromate (CrO_4^{2-}), selenate (SeO_4^{2-}), and arsenate (AsO_4^{3-}).

METHODS

Details of the tracer test, including sample collection and preservation, have been given in LeBlanc and others (Chapter B, this report). Ground-water samples were analyzed for MoO_4^{2-} using a modification of the colorimetric-thiocyanate technique. The limit of detection is approximately 50 µg/L (micrograms per liter) expressed as weight molybdenum (Mo). For the remainder of this paper, MoO_4^{2-} will be referred to as molybdate. Approximately 20,000 ground-water samples from the tracer test site have been analyzed for Mo to date.

Batch experiments were used to evaluate interaction between molybdate and sediment under controlled laboratory conditions. Two different samples were collected from wells adjacent to the tracer test and used in the batch experiments. Sample FSW 347-20 is from a well completed in freshwater above the sewage plume (field pH=5.55; specific conductance (S.C.)=45 µS (microsiemens)): sample FSW 347-46 represents ground water within the sewage contaminated plume (field pH=6.70; S.C.=250 µS). Sediment was collected at a depth of 1.2 to 1.5 m (meters) from a trench next to the tracer test. The material is medium to coarse sand and has visible coatings of iron oxyhydroxide.

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

Batch experiments were carried out in triplicate in 50 mL (milliliter) polyethylene centrifuge tubes. Sediment was preleached with the ground water to be used in a particular experiment to change the sediment pH to that of ground water. Thirty mL of ground water spiked with varying amounts of molybdate were added to 30 g (grams) sediment and the tubes placed on a rotating mixer at 0.7 revolution per minute. Preliminary data indicated that steady-state molybdate concentrations were reached within 5 days. All subsequent experiments were equilibrated for 7 days. After mixing, the sediment was allowed to settle for 15 minutes, then aliquots from each tube were withdrawn for pH and conductivity measurement. The solutions were then filtered (0.45 μm (micrometer)) and analyzed for molybdate.

RESULTS AND DISCUSSION

Laboratory Data

Data from batch experiments confirm that molybdate is reacting with the sediment. Isopleths for adsorption of molybdate from both contaminated and uncontaminated ground water are presented in figure B-2. Significantly more molybdate is removed from uncontaminated FSW 347-20 than from ground water contaminated by the sewage plume (FSW 347-46). The primary reason for this difference appears to be related to pH. After equilibration for 7 days, pH in tubes containing FSW 347-20 ranged from 5.6 to 5.8, compared with a pH of 6.6 to 6.8 for FSW 347-46. Increased adsorption of anions with decreasing pH is a well-known phenomenon and is primarily a result of increased positive charge on oxyhydroxide-coated particles. Adsorption of molybdate from FSW 347-46 appears to have reached a maximum of approximately 0.9 μg/g (microgram per gram), while molybdate adsorption from FSW 347-20 did not reach a maximum.

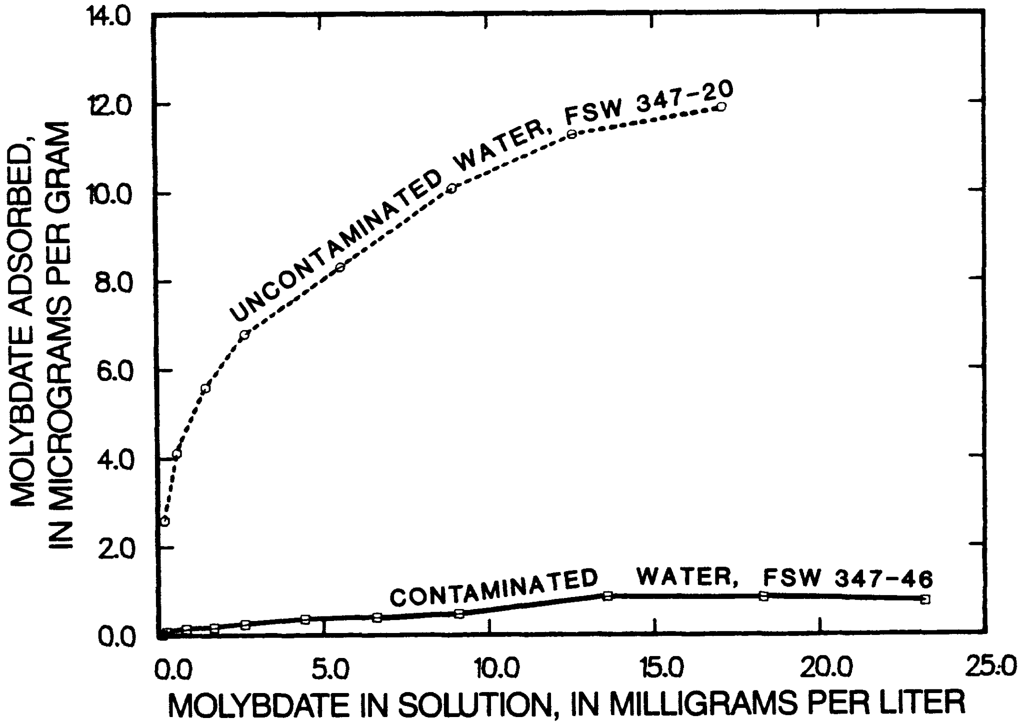

Figure B-2.—Adsorption isotherms for molybdate.

The effect of pH as well as ionic strength is seen in figure B-3. pH of both ground-water samples was adjusted with hydrochloric acid (HCl) or sodium hydroxide (NaOH); initial molybdate concentration was 5.0 mg/L (milligrams per liter). Adsorption of molybdate from both ground waters increased as pH decreased. Lower molybdate adsorption from FSW 347-46 is interpreted to be caused by anion competition. Chemical analyses of sewage-contaminated ground water have shown the presence of phosphate, an anion strongly adsorbed by iron oxyhydroxides. Also, the higher ionic strength of FSW 347-46 may result in less surface charge or a lower molybdate activity in solution.

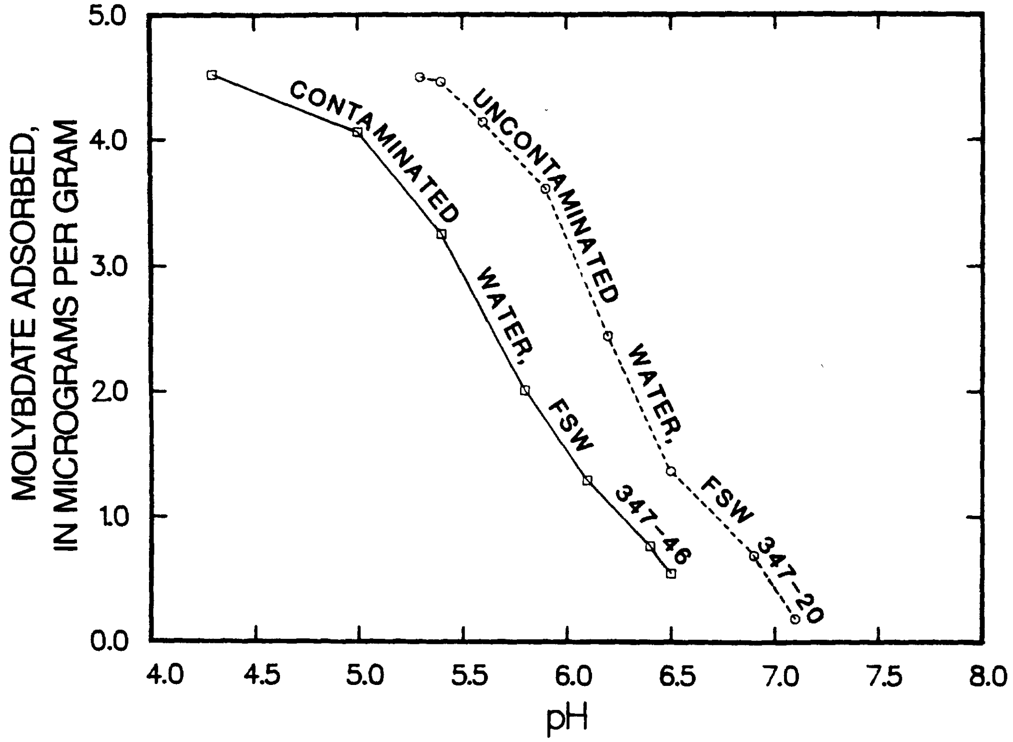

Figure B-3.—Adsorption of molybdate as a function of pH.

Dependence of molybdate adsorption on pH and solution composition has important consequences for modeling and explaining tracer test results. Specific conductance and pH profiles for three wells along the edge of the tracer test show significant vertical changes in ground-water chemistry (fig. B-4). It is apparent that any molybdate in the upper part of the tracer test will be adsorbed to a much greater extent. Most of the tracer "cloud" is below the low pH water. Values of pH in the majority of the tracer test area range from about 6.2 to 6.7 and specific conductance ranges from 190 to 350 μS. Based on data in figure B-3 (FSW 347-46), molybdate adsorption could vary from 0.4 μg/g (pH 6.7) to 1 μg/g (pH 6.2) at a specific conductance of 250 μS and an initial molybdate concentration of 5 mg/L.

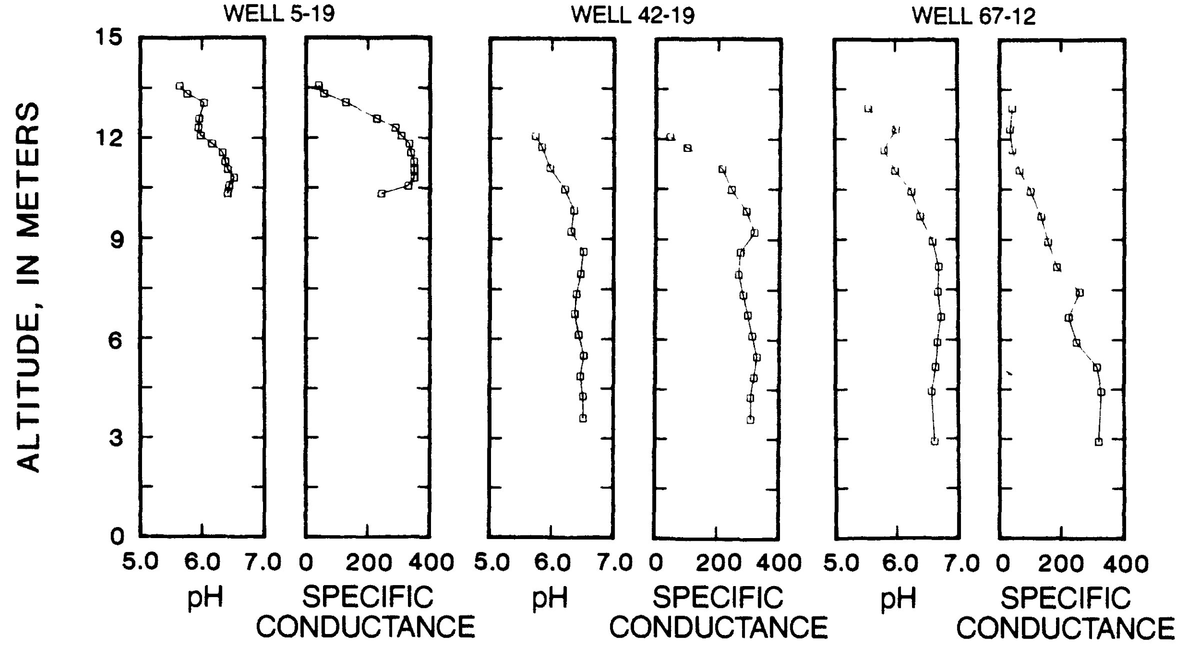

Figure B–4.—Variation of pH and specific conductance within tracer test area.

Field Data

Preliminary analysis of the December 1985 tracer test data by both areal depth-averaged and vertical cross-sectional contour plots are shown as figures B–5 and B–6. Contour plots of the data were made using a linear interpolation scheme as available through the DISSPLA[2] plotting routines. The limited number of data points available can cause questionable contouring results; however, the general profile is usually described in a reasonable manner.

Figure B–5 shows the depth-averaged concentrations of bromide (Br) (upper plot) and molybdate (lower plot). Locations of sampling wells are also noted on the plots. The maximum concentration of Br indicates that this conservative tracer has traveled approximately 70 m from the injection point. Several concentration maxima are evident within the overall plume. The molybdate concentration contours (lower curve of fig. B–5) lag behind Br and its average travel distance is approximately 50 m. Molybdate is retarded relative to the conservative Br by a factor of 0.72, implying molybdate reaction with the sediment.

Figure B–6 shows the cross-sectional (vertical) concentration profiles of the ions at wells located along the approximate center of the travel path of the respective tracers. Since more depth samples were available, and averaging was not necessary, better contour plots resulted. The Br data

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[2] Use of brand names in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

show two distinct maxima within the plume. One at 11-m altitude that has moved 76 m and one at 10-m altitude that has moved 53 m. Although not apparent from visual inspection of core samples, these data may indicate hydrologic characteristics that result in different ground-water velocities at different depths. The molybdate data show the same characteristics as the Br. The upper concentration maximum is at 11 m and has traveled 58 m. The lower maximum is at 10 m and has traveled 49 m. The vertical locations of the maximum concentrations are the same for both Br and molybdate; however, the relative distances traveled by each differ.

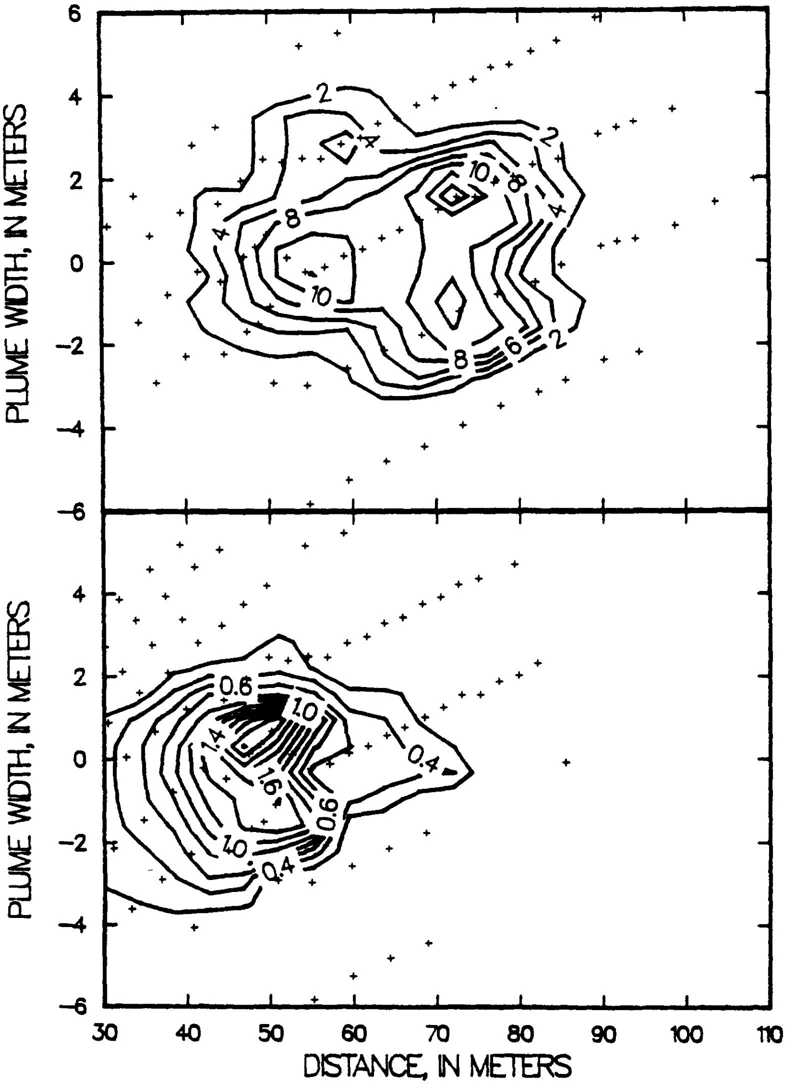

Figure B-5.—Depth-averaged concentrations (in milligrams per liter) of bromide (upper plot) and molybdate (lower plot) collected December 1985 at Cape Cod.

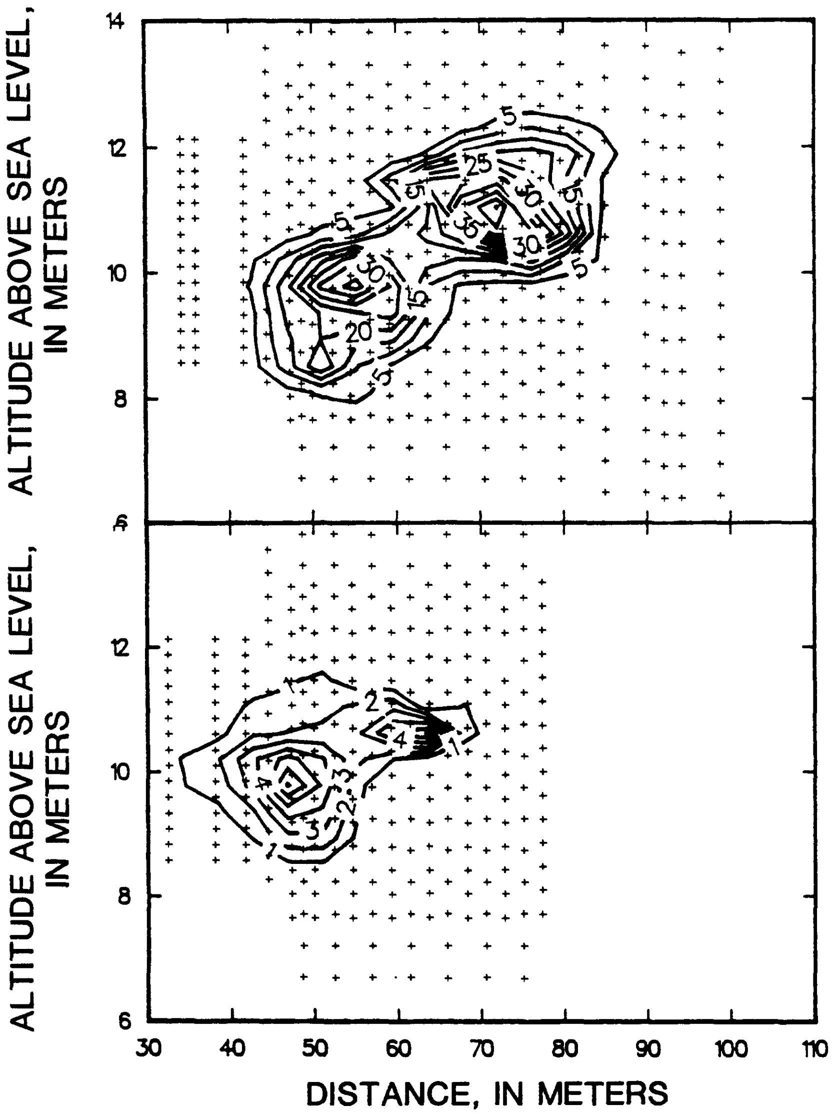

Figure B-6.—Vertical cross-sectional concentrations (in milligrams per liter) of bromide (upper plot) and molybdate (lower plot) collected December 1985 at Cape Cod.

The preliminary conclusions drawn from analyzing this one set of data show the problems in interpreting tracer results with limited data. Even for seemingly homogeneous material, vertical gradients in physical properties are present and can be masked during normal sampling procedures. Using these preliminary contouring results, the reactive tracer, Mo, was calculated to flow at velocities of 0.72, 0.76, and 0.91 times the Br velocities.

In summary, four factors have been shown to be important in predicting the transport of molybdate in the tracer test: (1) adsorption of molybdate increases with decreasing pH, (2) molybdate adsorption decreases as dissolved solids increase (primarily due to competition for surface sites with phosphate and possibly other anions such as sulfate), (3) the amount of molybdate adsorbed increases with solution concentration, and (4) variations in hydraulic conductivity affect the rate of molybdate transport in solution.

NATURAL-GRADIENT TRACER TEST IN SAND AND GRAVEL: PRELIMINARY RESULTS OF LABORATORY AND FIELD MEASUREMENTS OF HYDRAULIC CONDUCTIVITY

By Kathryn M. Hess[1], Steven H. Wolf[2], Denis R. LeBlanc[1],
Stephen P. Garabedian[1], and Michael A. Celia[2]

The relationship between aquifer heterogeneity and solute transport in a sand-and-gravel aquifer is being studied as part of the U.S. Geological Survey's toxic waste project on Cape Cod, Mass. Field tracer tests (Sudicky and others, 1983; Mackay and others, 1986; and Garabedian and others, Chapter B, this report) have shown that near the source, macrodispersion can deviate significantly from that predicted by Fick's law. This scale-dependent dispersion of solutes is believed to be caused by heterogeneity of aquifer properties. Gelhar and Axness (1983) have shown that dispersivity can be related stochastically to the variability of the hydraulic properties of the aquifer, in particular hydraulic conductivity. This stochastic theory is being applied to a three-dimensional distribution of hydraulic conductivity obtained from analysis of cores, in order to estimate dispersion in the glacial sand-and-gravel aquifer on Cape Cod. These results will be compared with field dispersivity values measured in the natural-gradient tracer test conducted at the site (Garabedian and others, Chapter B, this report).

Aquifer variability cannot be described exactly because it is impossible to measure hydraulic conductivity at every point. Instead, the variability must be described by determining the statistical properties of measured hydraulic conductivities, such as mean, variance, and spatial correlation. To define statistically the three-dimensional distribution of hydraulic conductivity at the tracer test site, continuous cores will be collected in about 40 borings. The target coring interval is the 6 m (meters) below the water table, the same interval through which the tracer cloud primarily traveled. In December 1986, the first set of cores was collected at 10 locations along a line which was 24 m long and parallel to the mean direction of flow observed in the tracer test, but offset 30 m to the west of the actual tracer path. Spacing between coring sites varied from 1 to 8 m, in order to facilitate the construction of a variogram of hydraulic conductivity from these 10 preliminary cores.

A fixed-piston, driven core barrel is used to obtain 1.5-m long, 5-cm (centimeters) diameter cores; recovery averaged 90 percent. Textural differences and cross bedding structure in the sand and gravel sediments seen in x-ray images of the cores are evidence that these cores are relatively undisturbed. A multiple port, constant-head permeameter has been developed to measure hydraulic conductivity over 8-cm intervals along the core.

Analysis of the initial set of cores will yield: (1) preliminary estimates of the geometric mean and the variability in hydraulic conductivity, and (2) correlation distances vertically and along the observed direction of ground-water flow. These results will be used to plan future coring. The geometric mean of hydraulic conductivities measured to date is 0.024 cm/s (centimeter per second) at 11 °C, the average ground-water temperature within the aquifer. Individual measurements of hydraulic conductivity vary an order of magnitude around the mean. The average hydraulic conductivity determined from an aquifer test conducted 2 km (kilometers)

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

[2] Department of Civil Engineering, Massachusetts Institute of Technology, Cambridge, Mass.

downgradient of the coring site is about 0.13 cm/s (LeBlanc and others, in press). The difference between these average values may result from local anisotropy, the small number of cores analyzed to date, or a true difference in hydraulic conductivity between the two sites.

The planned three-dimensional coring network offers the opportunity to compare permeameter measurements with other laboratory and field indicators of hydraulic conductivity, and to assess the value of each method for describing aquifer variability. Laboratory measurements include porosity and grain-size distributions; field measurements include geophysical and piezometer tests. Porosity and grain-size distributions will be measured on selected cores and compared to hydraulic conductivities. Ground-penetrating radar will be used to define large-scale structures, such as horizontal and dipping beds. Natural gamma and other geophysical logs of selected cored holes and cores will be correlated with laboratory profiles of hydraulic conductivity. Finally, piezometer tests will be conducted near the coring sites and the *in situ* values of hydraulic conductivity derived from these tests will be compared to those obtained in the coring program. The statistical description of aquifer properties at the tracer-test site obtained from the laboratory and field tests will be used to estimate the effects of aquifer heterogeneity on the macrodispersion of contaminants in the sand-and-gravel aquifer.

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DEVELOPMENT OF TECHNIQUES TO MEASURE *IN SITU* RATES OF MICROBIAL PROCESSES IN A CONTAMINATED AQUIFER

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

The distribution and intensity of microbial processes in ground-water systems have not been well characterized, despite growing evidence that micro-organisms affect the geochemistry of ground water. Part of the reason for this paucity of information is the difficulty in assessing whether a specific microbial process is actually occurring at a given site and its *in situ* rate of activity. In many cases, this is a direct result of the nature of the subsurface and the problems that arise in obtaining undisturbed and uncontaminated subsurface samples and the difficulties in maintaining *in situ* conditions during activity measurements. As part of an effort to delineate microbial processes in ground waters, studies were initiated at the U.S. Geological Survey Cape Cod Ground-Water Contamination site to determine the role of micro-organisms in inorganic nitrogen transformations in the subsurface. These studies have necessitated the development of specific methodologies to quantify the rates of these microbial processes, methodologies which should be generally applicable to studies of microbial processes in the subsurface.

The first approach employed was to match known physiological characteristics of certain groups of micro-organisms that mediate specific nitrogen transformations with the physical and geochemical components found within the different regions of the contaminant plume. The purpose was to identify the zones within which a given microbial process might be occurring. For example, a site located 0.3 km (kilometers) downgradient from the contaminant source (site F347) was identified as an area in which the occurrence of nitrate reduction (both dissimilatory nitrate reduction to ammonia and denitrification) was deemed likely. This conclusion was based upon detailed geochemical analyses of ground-water samples for dissolved oxygen (which inhibits both processes), nitrate (the substrate for both processes), ammonia, nitrogen, and carbon dioxide (the end products of the two processes), and nitrous oxide (an intermediate of denitrification). The results indicate a linear correlation between concentrations of nitrogen (N_2) and dissolved inorganic carbon (DIC). The ratio of DIC to N_2 was 1.6, which is nearly identical to the stoichiometric ratio (1.7) of carbon dioxide (CO_2) to N_2 production by denitrification.

The geochemical evidence is important as it indicates the zones in which a microbial or chemical process can occur and indicates the net results of these processes. The utility of this approach centers around the relative ease of sample collection and analysis, which allows investigation at a variety of sites and times. However, since the measurements are generally based on mobile chemical species, further measurements involving incubations with aquifer solids (and attached micro-organisms) must be conducted if the actual rate of a biogeochemical process at a specific site is required. One method we employed for qualitatively determining microbial activities involved sampling aquifer solids with a split-spoon corer, subdividing the sample, and assaying the freshly collected material in flasks. The assay itself may involve monitoring changes in the concentrations of

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

[2] U.S. Geological Survey, Menlo Park, Calif.

[3] Woods Hole Oceanographic Institute, Woods Hole, Mass.

products and substrates with time, or it may employ a tracer (such as ^{15}N), or it may involve a method unique to the activity of interest (such as the acetylene blockage technique for denitrification). The advantage of this approach is that a relatively large number of replicates is possible and it is also fairly easy to manipulate the assay conditions to test the effects of other parameters upon the activity of interest. Using these procedures, it was possible to demonstrate that nitrification, denitrification, and dissimilatory nitrate reduction were indeed occurring at site F347. The drawbacks of this approach are that the split-spoon core samples usually have lost most of the interstitial ground water, and hence, most of the necessary nutrients, and in the process the sample is exposed to air. Therefore, it is necessary to replace the lost ground water by making a "slurry" in the incubation flasks with ground water pumped from an appropriate depth and at the same time, attempting to restore the dissolved oxygen to its native level. The result of these manipulations is a large degree of uncertainty as to whether the rates exhibited in the flask incubations are indicative of *in situ* conditions.

In an attempt to overcome some of these limitations, a second procedure was developed to assay for microbial processes in whole cores. In this case, cores were taken with a piston corer that was designed and built by the University of Waterloo and which obtains a 1.5-m (meter) core with the interstitial ground water intact. This core can be cut into suitable-length subcores and microbial activities assayed directly within the intact core. At present, this technique is still in the developmental stages. It has been successfully employed to assay for denitrifying activity at site F347 using the acetylene blockage technique. Acetylene blocks the reduction of nitrous oxide to nitrogen and accumulation of nitrous oxide during the incubation is a measure of the denitrification rate. In this case, acetylene-saturated ground water was pumped into the cores with a peristaltic pump. The cores were incubated for 4 days at ambient temperature, after which the interstitial water was pumped out of the core and assayed for dissolved nitrous oxide. The results indicated that a zone of denitrifying activity was located 7 to 9 m below land surface, with a maximum at 8.9 m. This region corresponds to the zone suggested by the geochemical results. Samples were also taken from the 8.9-m depth and assayed with the slurry technique. These samples exhibited a rate more than fifteenfold higher than the direct core technique (31.2 versus 2.0 nanomoles nitrous oxide produced per gram dry sediment per day, respectively). The disadvantage of the direct core technique is that it is considerably more time consuming and costly than the slurry technique, hence, replication is more difficult.

The ultimate method to measure a subsurface microbial process is to assay the activity directly within the aquifer. This approach will most likely involve utilizing a tracer that can be injected into the aquifer. Several limitations are obvious, including time, cost, and the suitability of the tracer to be released into the environment. Nonetheless, it is essential that this type of experiment be conducted to serve as a standard against which new methodologies can be compared as they are developed. Therefore, an injection experiment using ^{15}N as a tracer at site F347 is in the formative stages. As part of the preparation for this experiment, an injection test using methane as a tracer was conducted and will serve to exemplify the approach. Ground water (100 L (liters)) taken from site F346 was amended with Freon-116[4], methane, and sodium chloride and injected back

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

into the ground into two ports of a multilevel sampler. Situated downgradient from the injection well were four multilevel sampling wells (1 m apart) located on a line perpendicular to local ground-water flow. Water samples were taken daily from these wells (total of 60 screened intervals) and assayed for the injectate components. The results demonstrated that all three components were transported at equivalent rates, the peak concentration of each arriving on the same day. When normalized to the injectate concentration, Freon-116 and chloride behaved identically, but methane was significantly attenuated. This attenuation was most likely the result of methane oxidation by the resident microbial population. The degree of attenuation can be used to calculate the amount of methane consumed, the rate of consumption, and the relationship between the amount of methane consumed and the methane concentration.

In summary, the methodologies presented here represent a concerted effort to develop techniques for quantifying rates of microbial processes in ground-water environments. To date, these techniques have only been tested in a sand-and-gravel aquifer, but these techniques should have at least some degree of applicability to other situations. No single technique is ideal, yet collectively they can provide a great deal of information about microbial processes in the subsurface.

TRANSPORT OF BACTERIA THROUGH A CONTAMINATED FRESHWATER AQUIFER

By Ronald W. Harvey[1], Leah H. George[1], Richard L. Smith[2], Denis R. LeBlanc[3]
Stephen P. Garabedian[3], and Brian L. Howes[4],

Bacterial transport through aquifers is presently the subject of considerable interest. Much research has been devoted to the movement of microbial pathogens through aquifers that supply drinking water, because the appearance of these organisms in well water has accounted for a majority of the reported outbreaks of waterborne diseases in the United States (Keswick, 1984). However, many factors controlling movement of pathogens through contaminated ground water are still poorly understood, and little is known about transport of indigenous bacteria that degrade organic contaminants in such aquifers. Since bacterial populations can require substantial acclimation times to degrade certain organic compounds, the fate of ground-water contaminants, particularly those that are persistent and highly mobile, may be affected by cotransport of bacteria through aquifer sediments. In addition to increasing the contact time between mobile contaminants and bacteria capable of degrading them, transport of bacteria could also be an important mechanism by which such organisms "seed" areas downgradient of contamination sources.

The ability of bacteria in ground water to be transported through aquifer sediments under a variety of hydrologic conditions and the role of bacteria transport in the distribution of free-living (unattached) bacteria within a 5-km- (kilometer) long plume of contaminated ground water is being investigated on Cape Cod, Mass. The contaminant plume at the Cape Cod site has resulted from on-land disposal of treated sewage over a 50-year period. Data suggest that transport of bacteria downgradient through aquifer sediments may be an important determinant of free-living (unattached) bacterial abundance within a part of the contaminant plume. For example, bacterial abundance within a 2-km-long zone beginning 0.4 km from the sewage disposal beds, varied linearly with changes in ground water specific conductance ($r^2=0.76$, $n=29$, $p \leq 0.001$). To examine bacterial transport under more controlled conditions, methodology was developed to collect and concentrate morphologically diverse populations of bacteria from the contaminant plume, label them with DNA-specific fluorochromes (fluorescent markers) and study their transport through aquifer sediments in ground-water tracer experiments. Potential effects due to surface characteristics and size upon transport were investigated using several types of bacteria-sized fluorescent microspheres, which were injected with the other tracers.

In the first type of test, a divergent (forced-gradient) tracer experiment, native ground-water bacteria were concentrated using tangential flow filtration, stained with 4',6-diamidino-2-phenlyindole (DAPI), and injected back into the aquifer along with conservative tracer (bromide) and 0.2, 0.7, and 1.2 μm (micrometer) (diameter) carboxylated microspheres. The microspheres are negatively charged at the pH of ground water at the test site. In this experiment, a radially divergent flow field was formed by continuous injection of water in a well at about 95 liters per minute. The tracers were added as a pulse to the injection stream and monitored as they moved with the radial flow past multilevel sampling devices located 1.7 and

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[1] U.S. Geological Survey, Menlo Park, Calif.

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

[3] U.S. Geological Survey, Boston, Mass.

[4] Woods Hole Oceanographic Institute, Woods Hole, Mass.

3.2 m (meters) from the injection well. The relative abundances of different sizes of fluorescent particles (microspheres and bacteria) changed substantially from point of injection to the closest sampling point, located 1.7 m from the injection well. Fractional breakthrough (C/C_o) of carboxylated microspheres at peak abundance at 1.7 m from the point of injection was related directly to particle size, that is, the larger the microspheres, the less the attenuation (immobilization caused by aquifer sediment particles) during transport. This result was qualitatively consistent with a colloid transport model describing the movement of minute particles through porous media, which predicts that 0.2 μm (diameter) particles would experience greater attenuation than would 0.7 μm and 1.2 μm (diameter) particles (Yao and others, 1971). Average microsphere diameter increased from 0.4 μm in the injectate to 0.6 μm at 1.7 m downgradient, suggesting a differential filtration effect. However, fractional breakthrough of DAPI-stained bacteria (0.2–1.6 μm long) was 100- to 300-fold higher than for the carboxylated microspheres, in spite of the overlap in size with the microspheres. The superior ability of bacteria to be transported through aquifer sediments relative to the microspheres is likely due to differences in surface characteristics. Peak breakthrough of DAPI-stained bacteria was nearly coincident with that of bromide at 1.7 m downgradient, but occurred 1.5 hours earlier than bromide at 3.2 m downgradient. This suggests a more direct average path of travel for bacteria than for bromide and may result from size-dependent exclusion of bacteria from the smallest, more tortuous interstitial spaces between sediment particles.

In the second type of tracer experiment, a small-scale, natural-gradient test, bacteria-sized fluorescent microspheres of differing diameters (0.23–1.35 μm) and differing surface characteristics were injected into the contaminant plume along with a conservative tracer (chloride). The tracers were injected as a pulse into a multilevel sampler and were monitored as they moved with the natural ground-water flow past a set of multilevel sampling devices located 6.9 m from the injection point. Preliminary results suggest that time to peak breakthrough at a sampling point located 6.9 m downgradient was largely dependent upon surface characteristics of the microspheres. Elapsed time between injection and peak breakthrough among types of microspheres in the 0.5- to 0.8-μm size class increased sequentially for the following microspheres: latex (neutral surface), polyacrolein (surface carbonyl groups), and carboxylated latex (surface carboxyl groups). Peak breakthrough of carboxylated microspheres occurred 8 days after that of uncharged microspheres, which suggests that the presence of surface carboxyl groups significantly retarded transport. Separation during transport of microspheres having different surface characteristics does not seem to result from size differences, inasmuch as peak breakthrough of 0.23-, 0.53-, and 0.91-μm diameter carboxylated latex microspheres occurred at approximately the same time.

The data from the two types of field experiments indicate that both surface characteristics and average diameter of bacteria-sized particles had substantial effects upon attenuation during transport, but that surface characteristics had the most significant effect upon retardation (time to breakthrough relative to chloride). This suggests that transport of bacteria through aquifers may depend, in part, upon nutrient conditions, inasmuch as levels of nutrients can affect both cell size distribution and surface characteristic (Fletcher and Marshall, 1982). Although the data also suggest that under certain conditions the mobility of some bacteria can approach that of a conservative tracer, the distance over which a bacterial population is likely to travel in a sandy aquifer would also depend upon the degree to which bacterial growth can offset losses caused by predation, sorption, filtration, and cell death, occurring during transport. In general, consideration of transport as one of the determinants of bacterial population dynamics resulted in a more accurate prediction of the distribution of free-living (unattached) bacteria in parts of the plume of sewage-contaminated ground water. Therefore, bacterial transport may play a role in the ultimate fate of organic compounds in at least some contaminated ground water.

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IMPORTANCE OF CLOSE-INTERVAL VERTICAL SAMPLING IN DELINEATING CHEMICAL AND MICROBIOLOGICAL GRADIENTS IN GROUND-WATER STUDIES

By Richard L. Smith[1], Ronald W. Harvey[2], John H. Duff[2], and Denis R. LeBlanc[3]

A large degree of homogeneity is often ascribed to subsurface environments. Consequently, ground-water monitoring wells are frequently spaced with little attention to potential vertical gradients of either chemical or biological parameters. However, vertical gradients can exist in ground water and especially in contaminated aquifers. These gradients affect the geochemical nature of the aquifer and therefore the microbial processes in the aquifer. The purpose of this study was to determine detailed vertical gradients of chemical and microbiological properties within the contaminant plume at the Otis Air Force Base toxic waste study site (Cape Cod, Mass.). The steepness of the gradients within the contaminant plume dictates the sampling intervals necessary for future work at this site, particularly for microbiological studies.

The site chosen for sampling is located near the core of the contaminant plume (LeBlanc, Chapter B, this report, fig. B-1, site F347) about 250 m (meters) downgradient from the sewage-disposal sandbeds (about 1.5 years traveltime for ground water). Situated at this location are four observation wells (5-cm (centimeter) diameter polyvinyl chloride (PVC) pipe), each with a 0.6-m long slotted PVC screen. The screens are set 6 to 10 m apart vertically (fig. B-7). Chemical data collected previously from these wells demonstrated that the shallowest well was screened in a zone of uncontaminated ground water and the three deeper wells were screened in the contaminant plume. The interval between the upper two wells, which includes the gradient between uncontaminated and contaminated ground water, was the zone chosen for detailed sampling in this study.

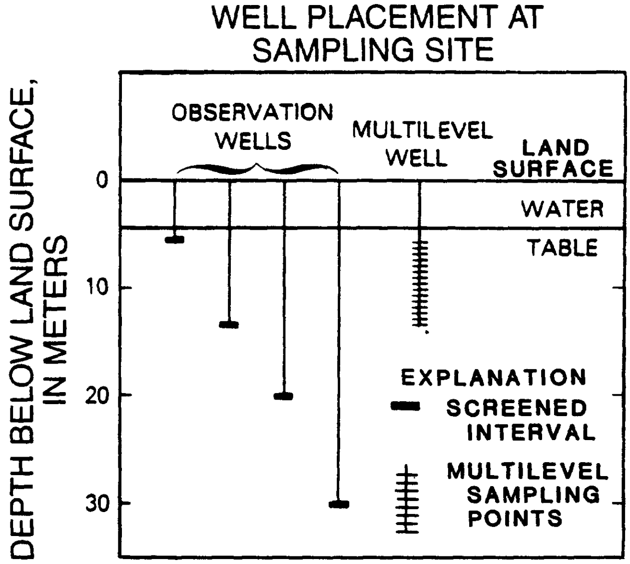

Figure B-7.—Well configuration at site F347.

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

[2] U.S. Geological Survey, Menlo Park, Calif.

[3] U.S. Geological Survey, Boston, Mass.

Detailed vertical sampling was done with a multilevel sampling device. This device has 15 ports spaced 0.6 m apart along an 8.5-m long section of 3.2-cm diameter PVC pipe. At each port, a 0.64-cm diameter polyethylene tube protrudes outside the PVC pipe through a hole and is capped with a nylon screen. Each tube extends to land surface inside the PVC pipe. Ground water was sampled from each port with a peristaltic pump. The placement of the multilevel sampler in the aquifer is shown in figure B-7.

Depth profiles of specific conductance (fig. B-8) and chloride (data not shown) exhibited steep vertical gradients. These constituents increased fourfold and ninefold, respectively, in the 2-m interval between 5.6 and 7.9 m beneath land surface. Below 10 m, the chloride concentration was constant with depth, while specific conductance decreased slightly. Nitrate concentrations also increased dramatically from 5.6 to 7.9 m (fig. B-9), but subsequently decreased with depth below 9 m. The entire nitrate-containing zone was undetected by the observation wells.

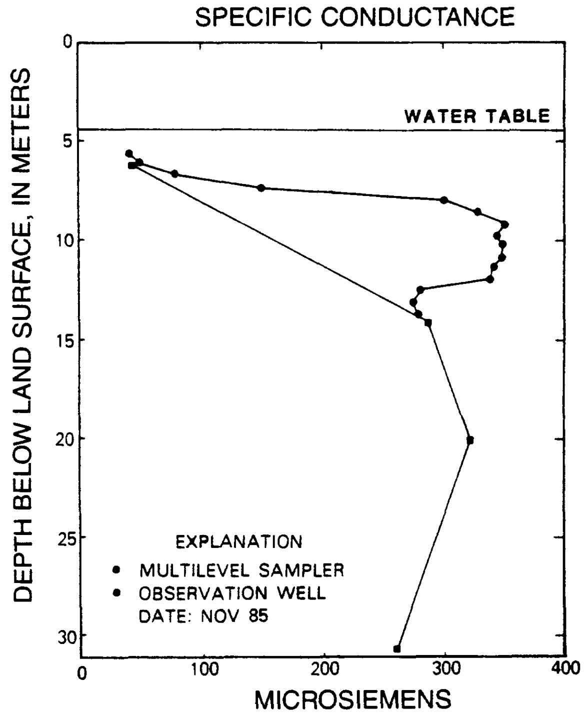

Figure B-8.—Depth profiles of specific conductance.

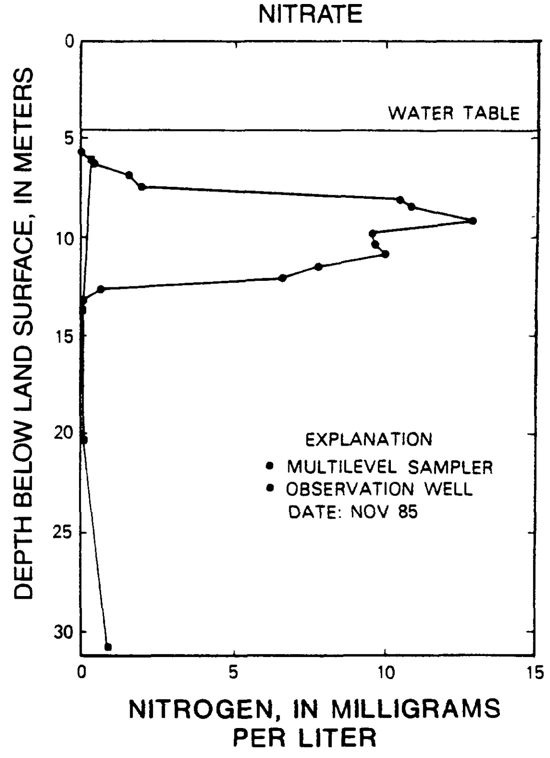

Figure B-9.—Depth profiles of nitrate.

Ground-water samples taken from the multilevel well also exhibited fine-scale variations in bacterial abundance and bacterial growth rates. Bacterial abundance increased 27-fold over background levels, reaching a maximum at 10.8 m below land surface (fig. B-10). Substantial changes in the bacterial community structure were evident across this gradient. The population changed from small, relatively uniform cells (average length 0.3 μm (micrometer)) to much larger, morphologically diverse organisms (average length 0.84 μm). Total cell biomass increased from 1.5 μg C/L (microgram of carbon per liter) at 6.1 m to 96 μg C/L at 14 m. Bacterial growth rates (frequency of dividing cells, fig. B-11) also increased over this depth interval, but not uniformly. Dividing frequency reached a maximum value at 12.6 m below land surface, which was twofold higher than the value for the observation well screened only 1.5 m below this depth.

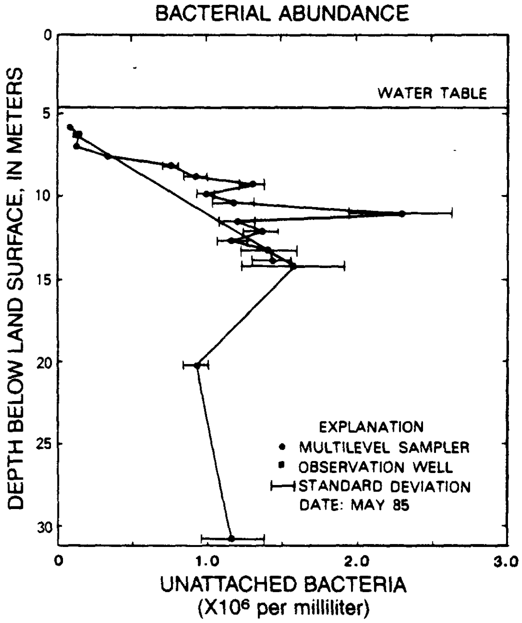

Figure B-10.—Depth profiles of bacterial abundance.

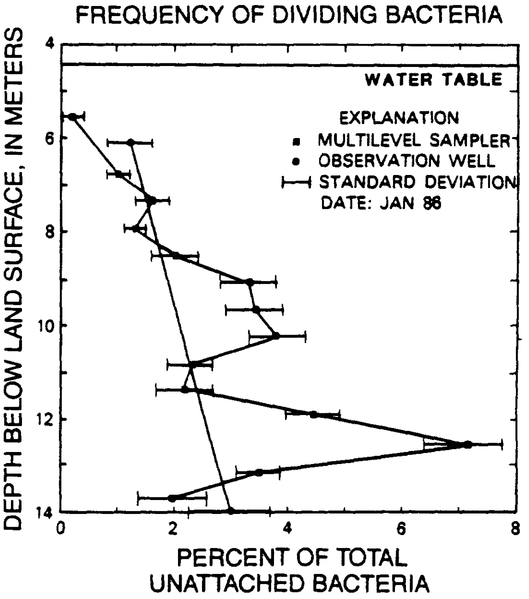

Figure B-11.—Depth profiles of bacterial growth rate (frequency of dividing cells).

The results of this study demonstrate that relatively steep gradients of chemical and microbiological properties occur in contaminated ground water. The detection of these gradients requires close-interval sampling. Otherwise, interpretation of data from only a few monitoring wells with screens set far apart vertically may yield incorrect conclusions about chemical and microbiological processes in the aquifer.

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A CONCEPTUAL CHEMICAL PROCESS MODEL FOR SEWAGE CONTAMINATION OF A SAND AND GRAVEL AQUIFER

By E. Michael Thurman[1]

A one-dimensional chemical process model was developed for the zones of contamination that have occurred over the past 50 years in ground water downgradient from the Otis Air Force Base sewage treatment plant. The conceptual model applies an expert system approach (heuristic knowledge) using a knowledge base from four types of information: hydrology, source history, solute behavior, and chemical and microbiological zones inferred from the field chemical data for 1978 to 1985. The model uses the combined information from recent research efforts of LeBlanc (1984) and other researchers (Chapter B, this report).

The purpose of the conceptual model is to reconstruct various zones of contamination from 1936 to the present and to predict the distance downgradient from the sandbeds for the leading edge of all chemical solutes. Furthermore, the conceptual model is useful to test plume relationships among solutes, and it has given us new ideas for future research, as well as immediate experiments that may be done to clarify our understanding of the plume chemistry. The conceptual model is especially useful for interpreting the many field measurements of plume chemistry.

The conceptual model considers chemical and microbiological processes including: ion exchange of potassium, phosphate, and ammonium; sorption of tetrachloroethylene (TCE), dichlorobenzene (DCB), and alkylphenol; and biodegradation of ammonium, nitrate, and surfactants (alkyl benzene sulfonate (ABS)). The one-dimensional conceptual model has a number of simplifications and assumptions. Hydrology is simplified to plug flow, the distribution coefficients (K_d) are estimated from field relationships, lab experiments, and a divergent tracer test. Time of entry or source history of compounds was estimated from chemical records, plant usage, and the literature of waste disposal. The output of the model is best viewed as a series of cross sections of the plume chemistry, manually constructed as zones of contamination, from examination of all chemical data and process information.

We used the model by taking the best estimate of average ground-water velocity and direction of flow and predicting the plumes of contamination with source history and chemical and microbiological processes superimposed. The model was run from 1936 to 1985 examining 5- to 15-year intervals for location and interrelationships of zones of contamination. Field data from 1979–80, 1983, and 1985 were used to calibrate the model. The diagrams for the model were constructed with the help of a simple computer spreadsheet, Lotus 1–2–3[2].

The screen display for the spreadsheet is called a template (table B–1). The year of prediction was entered into the template, along with the ground-water velocity, and the spreadsheet calculated the distance downgradient for all the chemical solutes listed. The spreadsheet allows the user to select three variables to manipulate the solute transport. They are: year of entry (YOE), distribution coefficient (K_d), and average ground-water

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

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

velocity. The information entered into the template can also be varied for year of prediction. The model was calibrated using the best chemical data for chronology of the plume, which are tritium for wells F294 and F375 at the toe of the plume, and the methylene blue active substance (MBAS), alkyl benzene sulfonate (ABS), and linear alkylbenzene sulfonate (LAS) measurements in different zones, from wells F262 to F410. The three variables were manually varied within the range of possible values, and the user cross verifies the data to find logical inconsistencies in the results. When more than several inconsistencies are found, the variables are changed to get the best fit overall of the chemical species within the confidence limits of the data.

Table B-1.—*Example of spreadsheet template completed for 1985 prediction*

Year of prediction: 1985
Velocity: 0.27 meter per day

Solute	Predicted transport distance (meters)	Year of entry	Distribution coefficient
Nitrate	4,900	1936	0
Ammonia	1,900	1936	.3
ABS-surfactant	3,500	1950	0
LAS-surfactant	2,000	1965	0
Tetrachloroethylene	1,400	1971	0
Boron	3,500	1950	0
Alkylphenol	430	1959	1.0
Tritium	3,100	1953	0
Phosphate	430	1936	2.0
Potassium	1,900	1936	.3
Dichlorobenzene	3,500	1950	0
Sodium, calcium, and magnesium	4,900	1936	0

The output from the spreadsheet may be viewed rapidly with the graphical program in the spreadsheet. For example, figures B-12 through B-14 are spreadsheet graphs showing predictions for 1950, 1965, and 1985, respectively. The graphs are immediately updated to the screen after changing any of the three variables and requesting "graph." The rapid access to graph gives quick insight into the relationships of the data. For example, by viewing figures B-12 through B-14, it was noted that the ABS plume had to pass through the core of ammonium, potassium, and phosphate from 1950 to 1985, whereas, ABS did not pass through the core of the TCE plume; thus, important relationships may be quickly noted by the graphical display of the spreadsheet program.

The most significant finding was that average ground-water velocity for this sampling analysis was considerably slower than hydrologic data indicated, from 0.24 to 0.34 m/d (meter per day), rather than 0.30 to 0.46 m/d as shown by hydrologic studies (LeBlanc, 1984). The velocity data were fitted with the tritium and ABS chemical data and well defined YOE. We are presently considering what may be the causes for the discrepancy in velocity between chemical and hydrologic data.

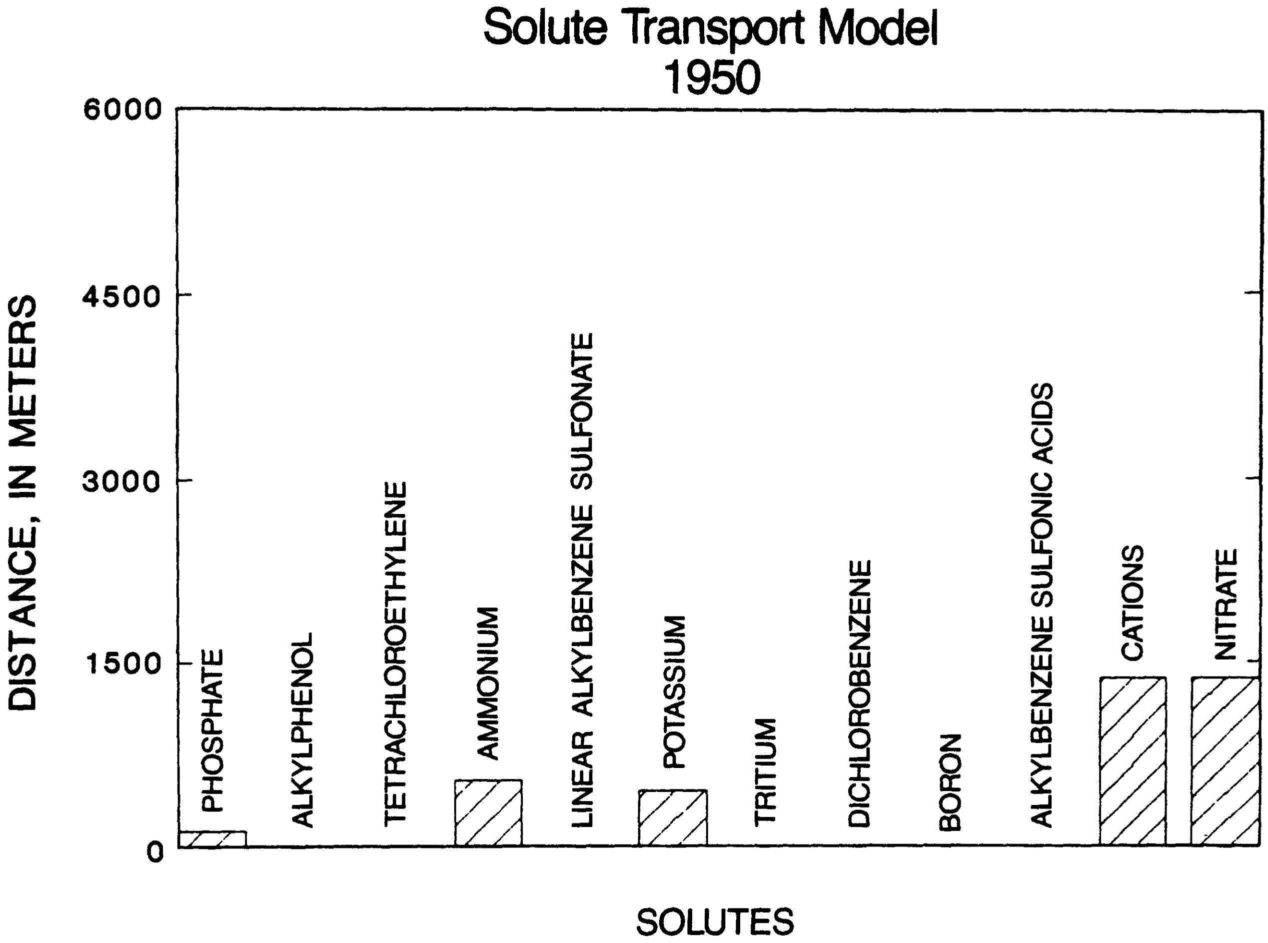

Figure B-12.—Solute transport model predictions for 1950.

The conceptual model also suggested interesting questions on plume chemistry. For example, the large zone of volatile organic contamination at well F254 does not fit with an early time of entry (1950). Rather, the model predicted a much later entry time, about 1970. Records on waste disposal have recently been found that show solvents, such as TCE, were disposed of during the early 1970s at the sewage plant, which is evidence that the model's prediction may be correct.

Another question was the zone of mixing between ammonium and nitrate at well F262. The model predicted that the ammonium should be much further downgradient than it actually is. Nitrification (conversion of ammonium to nitrate by microbes) is probably responsible for this difference in ammonium transport. However, the zone of mixing between nitrate and ammonium is interesting for another reason. Dispersion at the mixing front of ammonium and nitrate causes dilution of ammonium, which increases the sorption and increases retardation of ammonium (because of a nonlinear isotherm). On the other hand, dispersion puts oxygen into the mixing zone, which allows for nitrification and removal of ammonium. Because nitrate moves at least twice as fast as the low concentrations of ammonium, we ask the question, which process is most important and controls the transport of the ammonium front? The answer is not clear from the conceptual model, and this question is being addressed by Kipp with a one-dimensional solute transport model (Chapter B, this report).

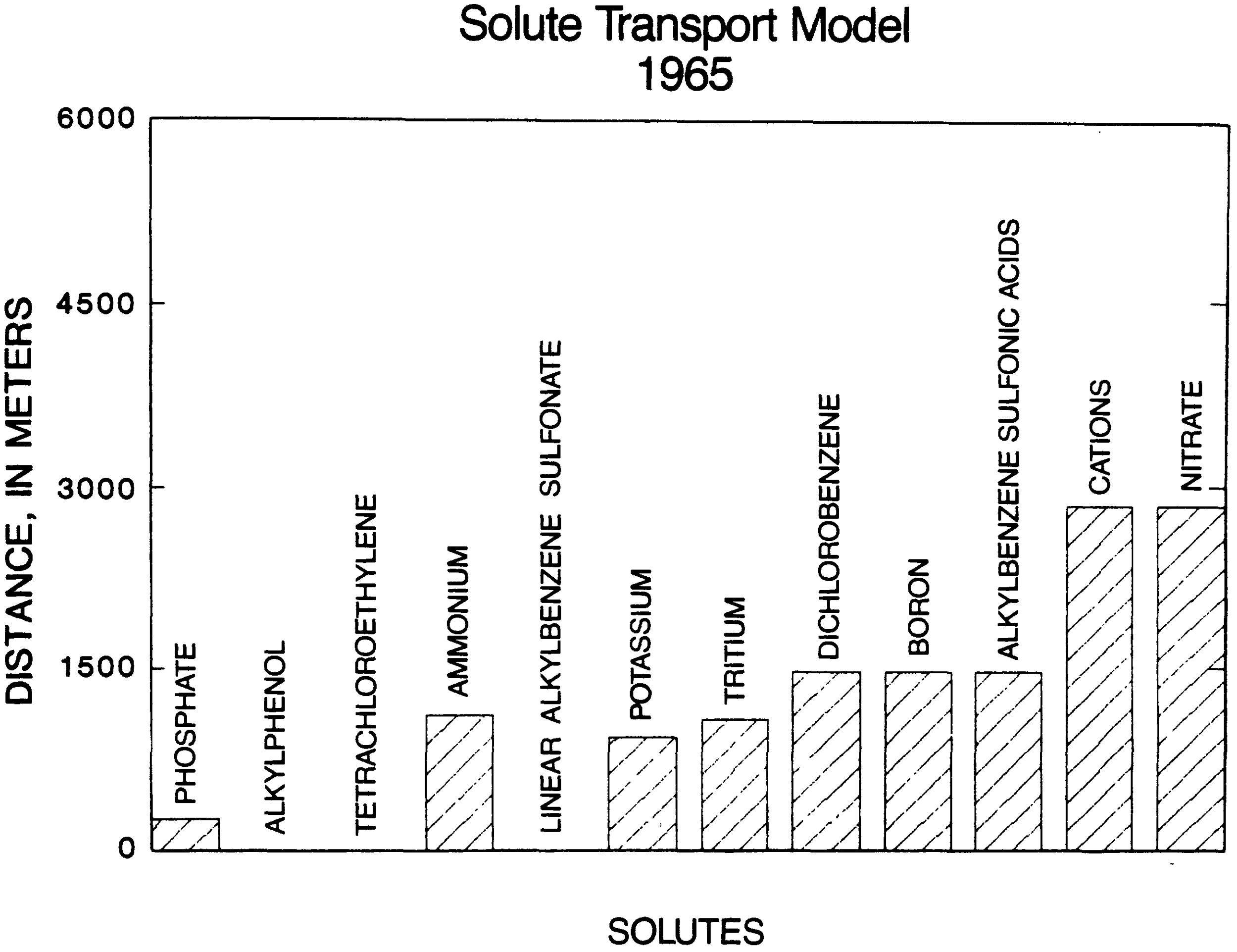

Figure B-13.—Solute transport model predictions for 1965.

The spreadsheet graphs also show that nitrate concentrations just downgradient of the ammonium zone are limited by oxygen concentration, shown in the equation below:

$$NH_4^+ + 2O_2 = NO_3^- + 2H^+ + H_2O \quad (1)$$

However, in downgradient wells (F282 and F375) nitrate may be higher because of other sources of nitrate (early release from the plant). These sources of nitrate are hypothesized in the conceptual model.

The conceptual model also predicts a snowplow effect for the major cations (calcium, sodium, and magnesium), which is the result of the ion exchange release of these cations from the aquifer solids when ammonium sorbs. Potassium is also released, but competes with ammonium for sorption sites. The model predicted that the potassium/nitrate ratio goes to zero, as nitrate separates from the snowplow front of potassium at the toe of the plume.

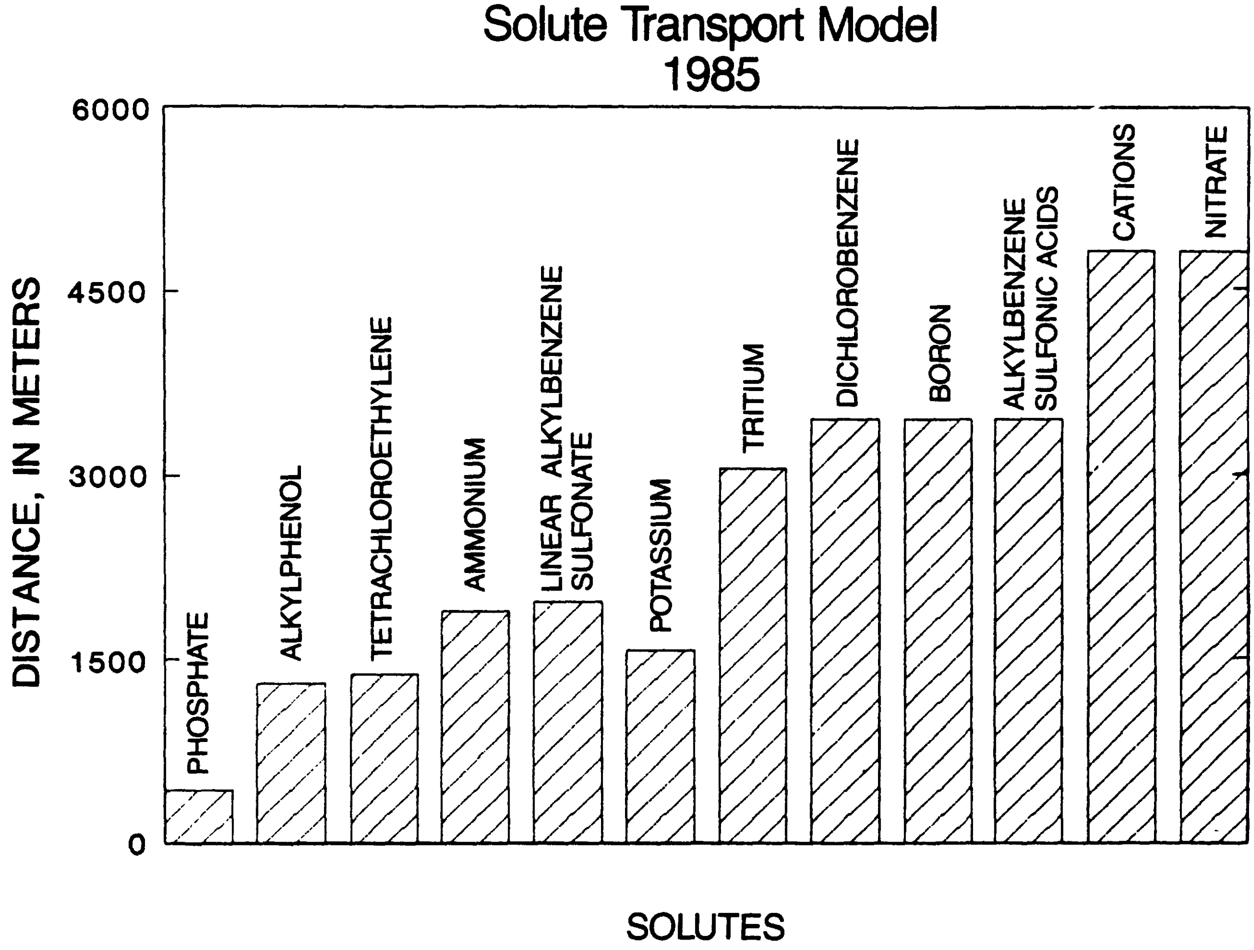

Figure B-14.—Solute transport model predictions for 1985.

Finally, based on the results of the conceptual model, the following experiments to better understand the plume are being conducted or are being planned:

- NH_4-NO_3 transport is being modeled by a one-dimensional solute transport model,
- Drilling and chemical analysis are being planned to locate the K-NO_3 front at the toe of the plume,
- Divergent tracer tests are planned to examine the conservative nature of boron and ABS-LAS in more detail,
- More detailed hydrologic tests are planned to test the slower average velocity predicted by the model,
- Measurements of the relationships of tritium and ABS at well F375 are planned to clarify YOE and allow for better use of the spreadsheet,
- Laboratory measurements of K_d for TCE and DCB are planned to clarify YOE for TCE, and
- 1987 predictions are being made for tritium, boron, and ABS, which can be tested at the furthermost well (F375) to calibrate the spreadsheet for more complex one-dimensional solute transport models.

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PRELIMINARY ONE-DIMENSIONAL SIMULATION OF AMMONIUM AND NITRATE IN THE CAPE COD SEWAGE PLUME

By Kenneth L. Kipp[1]

Ammonium and nitrate contamination plumes in the ground water extend downgradient from the Otis Air Force Base sewage treatment plant on Cape Cod, Mass. The nitrate plume is observed at least 1,300 m (meters) beyond the end of the ammonium plume. The hypothesis that conversion of ammonium to nitrate is taking place dates back to the first study at this site. Plots of the ammonium plume in one dimension along the axis of maximum concentration show little change in extent from 1978 to 1986. Such a steady-state profile indicates a reaction mechanism that consumes ammonium.

A simple, one-dimensional solute transport model was formulated to determine if a reasonable set of transport and reaction properties could account for the observed ammonium and nitrate concentration profiles assuming a linear reaction for the conversion of ammonium to nitrate. The model employed analytical solutions to the one-dimensional solute-transport equations for ammonium-nitrogen and nitrate-nitrogen, with constant, uniform properties along the flow path. The transport mechanisms included advection, dispersion, equilibrium sorption, and linear reaction. The flow path for the one-dimensional solute transport was along the line of maximum observed contamination, from beneath the infiltration beds to well F182, about 3,900 m downgradient in the saturated ground-water system. The source term at the beginning of the flow path was a specified, constant ammonium-nitrogen concentration. Observed temporal variations in ammonium and nitrate profiles along the first quarter of the flow path indicate source variations. Because these variations could not be estimated, the first quarter of the flow path, from under the treatment plant infiltration beds to well F254, was excluded from this preliminary transport model. This exclusion is the most unrealistic component of the transport model formulation. The only source of nitrate-nitrogen along the flow path was assumed to be the decay of ammonium. The intermediate species, nitrite, was not modeled explicitly because the observed nitrate-nitrogen concentrations include nitrite-nitrogen.

Spatial profiles of ammonium-nitrogen and nitrate-nitrogen were calculated over a range of time from plant startup to the present. The cases of reaction in both phases and reactions only in the flowing phase were considered. Optimum sets of transport and reaction properties were determined by using a least-squares fitting procedure that resulted in the best match of the present, observed ammonium-nitrogen profile. The optimum values were: dispersivity, 1.5 to 3 m, equilibrium sorption coefficient, 0.2 milliliter per gram; reaction rate constant, 1.8 to 3.6×10^{-4} d^{-1}; and elapsed time, 25 to 32 years. These values were within ranges estimated from other information except for the reaction rate which was a factor of 10 smaller. An abbreviated sensitivity analysis showed that the computed ammonium-nitrogen profile was most sensitive to the reaction rate constant and least sensitive to the dispersivity value.

The calculated nitrate-nitrogen profile associated with the optimum calculated ammonium-nitrogen profile contains nearly a factor of 10 too much nitrogen. This excess suggests that either: (1) there is a mechanism for denitrification nitrate that has not yet been identified, or (2) there is

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

not a complete conversion of ammonium to nitrate. It is not likely that lateral or vertical transport away from the flow path of the maximum concentration could reduce the nitrate-nitrogen concentrations to the values observed. The second hypothesis is consistent with the assumption that the conversion is limited by the supply of oxygen in the saturated ground water. But then there needs to be a mechanism for the disappearance of unconverted ammonium or it would be transported down the rest of the flow path. Further work is needed to resolve this mass imbalance between ammonium-nitrogen and nitrate-nitrogen in the contamination plume.

This preliminary transport simulation has indicated several avenues for further investigation that illustrate the benefits of simple modeling calculations while the field study is in progress. More sophisticated transport models can be employed as the amount of data and understanding of the system increase.

INFLUENCE OF GEOCHEMICAL HETEROGENEITY IN A SAND AND GRAVEL AQUIFER ON THE TRANSPORT OF NONIONIC ORGANIC SOLUTES: METHODS OF SEDIMENT CHARACTERIZATION

By Larry B. Barber, II[1]

The results of the first 3 years of research into the organic geochemistry of the contaminant plume at the Otis Air Force Base (OAB) site suggests that sorption of hydrophobic organic compounds has resulted in the retardation of their transport (Barber, 1985; Barber and others, in press). In order to develop a better understanding of the sorptive processes controlling the transport of organic compounds at OAB, detailed characterization of the variability in sediment geochemical parameters is being conducted.

The influence of solid aquifer materials on the subsurface transport of dissolved anthropogenic organic chemicals is an area of considerable research activity. Sorption (partitioning) of nonionic organic solutes onto natural sediments has been shown to correlate with the bulk organic carbon content of the sediments, for sediments with high (>0.10 percent) organic carbon (Karickhoff and others, 1979; Means and others, 1980; Chiou and others, 1981; 1984; Schwarzenbach and Westall, 1981; Nau-Ritter and others, 1982; Karickhoff, 1984; Schellenberg and others, 1984). However, in low-organic carbon sediments (<0.10 percent) which characterize sand-and-gravel aquifers such as at OAB, the relation between the sorptive nature of nonionic organic compounds and sediment properties is not as clear (Mingelgrin and Gerstl, 1983; Banerjee and others, 1985; Mackay and others, 1986). Chiou and others (1985) have shown that there is a strong mineralogical control on the sorption of nonionic organic compounds in dry soil, but the sorption onto mineral surfaces is significantly inhibited by the presence of moisture. Their work suggests that direct mineralogical interactions with the organic solutes should be negligible in water-saturated aquifer systems. However, it has been observed that for sediments with low levels of organic carbon, the retardation of subsurface transport is frequently quite significant (Roberts and others, 1982; Curtis and others, 1985, Freyberg, 1985), suggesting that when little carbon is present, mineral interactions may become important in the sorption of organic solutes. This is particularly true for compounds capable of hydrogen bonding (Isaacson and Frink, 1984). Clays are generally inferred as the mineral components with which organic solutes can interact in soils (Karickhoff, 1984); however, many high-permeability aquifers have very low clay contents.

The sorptive capacity of a sediment for nonionic organic solutes increases with decreasing particle size, and maximum sorption tends to occur in the <125-μm- (micrometer) size fraction due to increases in the organic carbon and clay content, and surface area (Boucher and Lee, 1972; Karickhoff and others, 1979; Schwarzenbach and Westall, 1981). Since sorption of nonionic organic solutes to aquifer material is primarily a function of the organic-carbon coatings on the mineral substrate, it is of interest to determine if the carbon content is a function of nonclay mineralogy. If it is, then the effective distribution of such minerals and their heterogeneity within the aquifer can potentially play a role in the subsurface transport of organic pollutants. The same sedimentary heterogeneity that can control the distribution of minerals within an aquifer also has the ability to retard transport based solely on hydrological properties (Gillham and others, 1984).

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

Accessory minerals such as garnet, magnetite, amphiboles, and micas tend to occur as small particles due to magmatic crystallization relations; thus, their abundance is generally greater in the fine fraction. Because of the surface properties and weathering characteristics of many accessory minerals, it is possible that their surfaces will be enriched in organic carbon relative to quartz and feldspar. This assumption is based on zero point of charge (zpc) considerations (Parks, 1975; Stumm and Morgan, 1981). The zpc of quartz and feldspar is about 2.0, so that at the pH of most ground-water systems (5–8), the surface will be negatively charged. Because of the abundance of negatively charged functionalities in natural dissolved organic matter (Thurman, 1985), quartz and feldspar surfaces may not be enriched in organic carbon as the result of charge repulsion. Some minerals such as magnetite and other oxides have zpc values greater than 7.0 and will be positively charged under most ambient pH conditions, and will have greater potential for adsorption of dissolved organic carbon (Davis, 1982). Minerals with greater amounts of organic matter associated with them as grain coatings should have enhanced partitioning of nonionic organic compounds. If a particular mineral has a high affinity for natural organic carbon, it may contain the majority of the sediment organic matter while only comprising a small fraction of the bulk sediment. As a result, the effective distribution of a particular mineral fraction may exhibit important control on transport.

Most investigations of the sorptive properties of sediments classify the material according to particle size, fraction organic carbon, surface area, clay content, and cation exchange capacity. However, such descriptions give little insight as to the mineralogical composition of the material, or to the potential sites of sorptive interaction. This investigation will evaluate the role of geochemical and mineralogical heterogeneity at the OAB site on the sorption and transport of nonionic organic compounds, by: (1) characterizing the spatial variability of mineralogy and grain coatings (organic and inorganic), (2) evaluating the sorptive properties of the various mineral components, and (3) determining the petrographic relationships of the various geochemical components. This research should provide data on the actual sites and mechanisms of nonionic organic solute sorption in ground-water systems.

The initial focus of this study was to develop a protocol for collecting and subsampling aquifer sediments, characterizing the heterogeneity of the sediment geochemistry and mineralogy, and obtaining relatively pure mineral isolates for sorption experiments. Figure B–15 presents a subsampling scheme for characterizing geochemical heterogeneity in unconsolidated aquifer sediments. The aquifer material is collected as continuous core intervals (using a device developed at the University of Waterloo) at multiple sites located from the infiltration beds downgradient, including sediments from both within and outside the influence of the contaminant plume. The sediments are fractionated based on particle size by standard sieve analysis to facilitate further processing of the material, and to allow for correlation with other studies from the literature. The mineralogy of each size class is then determined by petrographic microscope and x-ray diffraction methods. The relative abundance of each mineral component is determined by point-counting methods using epoxy-impregnated thin sections of each size class. An undisturbed part of each core is retained and epoxy impregnated for petrographic fabric analysis and evaluation of the effective distribution of the various mineral components.

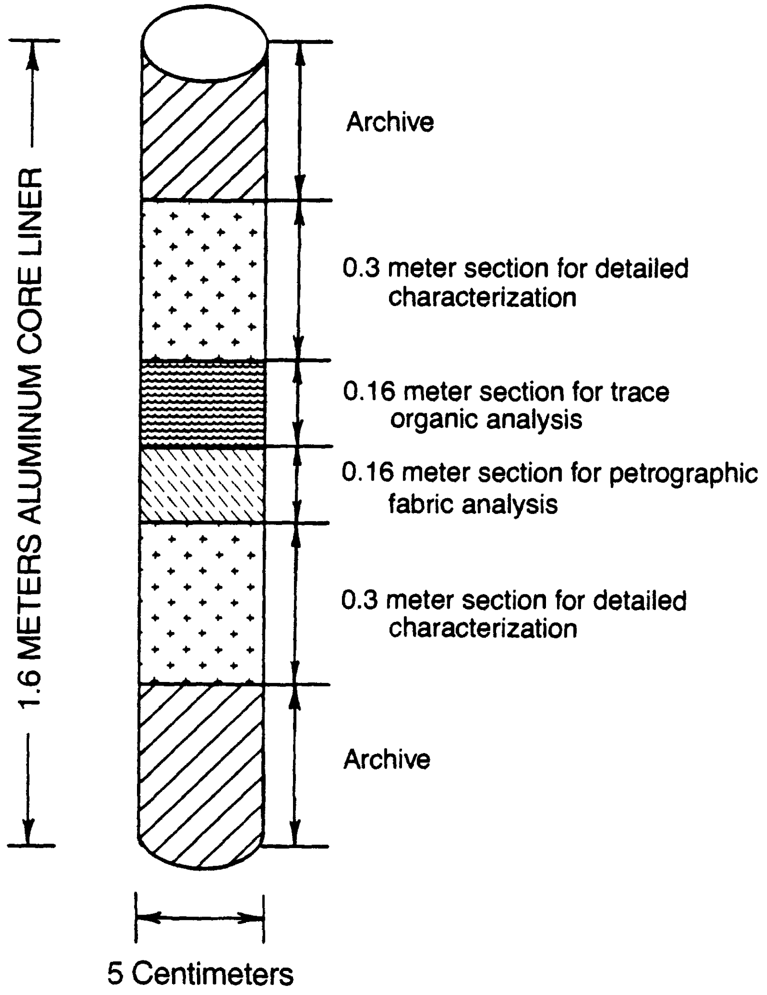

Figure B-15.—Subsampling scheme for characterizing geochemical heterogeneity in Otis Air Force Base aquifer material.

The suite of minerals within each particle-size class is then separated into groups of relatively pure mineral constituents based on magnetic susceptibility and density. Magnetic separations are performed using a Franz[2] magnetic separator in which a fine stream of air-dried material of uniform size is fed into a strong magnetic field. By varying the strength of the magnetic field and the forward and side slope of the feed chute, mineral fractions of high purity can be obtained. The density separation is carried out on a Wilfley table in which a fine stream of sieved material is washed onto a vibrating corrugated table with a slope. As the sediments are washed across the table, the lapping action rapidly washes low-density minerals off the edge of the table whereas high density minerals stay on the table and are collected as they dribble off the end. Table B-2 lists the advantages and disadvantages of the two methods. This separation scheme results in

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

relatively simple mineralogical fractions such as magnetite, garnet/staurolite, and quartz/feldspar. The relative distribution of the various mineral constituents are determined from the separates, and used to characterize geochemical heterogeneity within the aquifer. A major objective of the mineral separation scheme is to obtain sufficient quantities of relatively pure natural mineral components for detailed experimental studies (batch and column) of their sorptive properties.

Table B-2.--*Comparison of Franz magnetic separator and Wilfley density separation table for the separation of minerals*

Separator	Disadvantages	Advantages
Franz magnetic	Relatively slow (less than 500 grams per day).	Does not involve washing the sediments. Provides high purity isolates.
Wilfley density	Relatively poor separation.	Can process large samples rapidly (kilograms per hour).
	Requires extensive washing.	Removes all fine materials on major size fraction.
	Requires further separation.	Good method for preconcentration for the magnetic separation.

Each of the bulk sediment fractions, as well as each mineral isolate, is analyzed for organic carbon and inorganic grain coatings by various chemical and instrumental methods. Surface area, surface charge, and cation/anion exchange capacities are also evaluated. The detailed characterization and experimental data will allow us to determine if there are mineralogical controls on nonionic organic solute sorption.

The sediments that comprise the Otis aquifer material consists of glacial outwash derived from igneous and metamorphic source rocks (McMasters and Garrison, 1966). The aquifer material consists predominantly of discrete mineral grains in the sand and finer fractions, whereas sediments coarser than sand are dominated by rock fragments consisting of aggregates of minerals. Table B-3 summarizes the major minerals comprising the sand fraction of the OAB sediments. This investigation is primarily concerned with the sand and silt fractions which account for approximately 90 to 95 percent of the aquifer (fig. B-16), and is the proposed site of major sorptive interaction. The mineralogical composition of the various size fractions systematically changes, with the abundance and complexity of trace minerals increasing considerably with decreasing particle size, whereas quartz and feldspar decrease in relative abundance. Conversely, the mineralogy in the coarse to medium-sand fraction is predominated by quartz and feldspar, with only a minor amount (<5 percent) of accessory minerals. Only trace amounts of clays are present (<0.1 percent.)

Table B-3.—*Major mineral constituents present in the sand and silt sized fraction of the Otis Air Force Base aquifer sediments*

[Mineral identification made by petrographic microscope methods]

Major minerals[1]	Accessory minerals[2]		
Quartz	Apatite	Glauconite	Muscovite
Orthoclase	Augite	Hornblende	Rutile
Plagioclase	Biotite	Hematite	Sillimanite
	Chlorite	Ilmenite	Sphene
	Corundum	Kayanite	Staurolite
	Epidote	Limonite	Tourmaline
	Garnet	Magnetite	Zircon

[1] Comprises approximately 90 percent of the material.
[2] Comprises approximately 10 percent of the material.

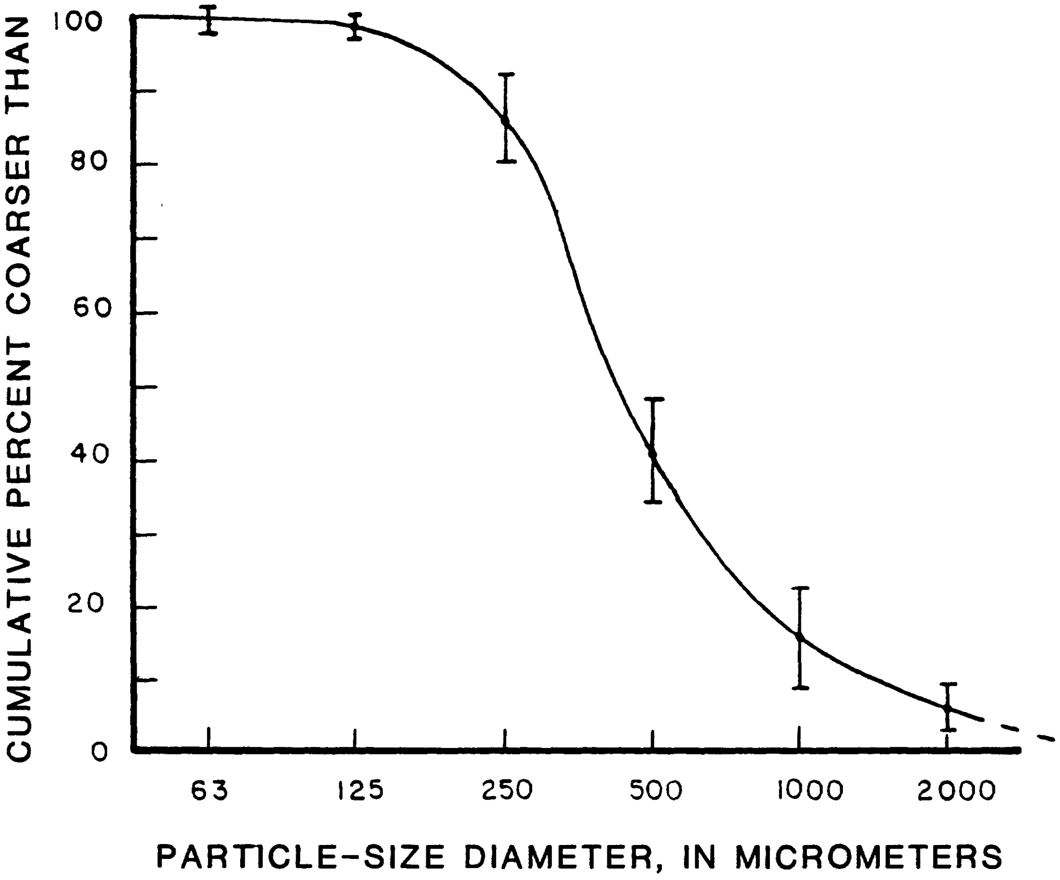

Figure B-16.—Particle-size distribution for five 0.3 meter core samples. Error bars are ±1 standard deviation.

The organic carbon content of the sediments increases with decreasing particle size (table B-4). For a given size fraction, the organic carbon is significantly higher in the magnetically susceptible mineral isolate than in the nonmagnetic fraction (quartz and feldspar). These preliminary data suggest there is a mineralogical control on the distribution of organic carbon within the bulk sediment; thus, there is also probably a mineralogical control on sorption interactions.

Table B-4.—*Total organic carbon values for the 125 to 250 and <63 micrometer particle sizes with and without magnetic separation*

Particle size (micrometers)	Percent organic carbon[1]	Standard deviation
125-250 (total)	0.015	0.003
125-250 (nonmagnetic)	.015	.003
125-250 (magnetic)[2]	.059	.005
<63 (total)	.049	.001

[1] Determined by high temperature oxidation and coulometric detection.

[2] The magnetic fraction comprised 3.5 percent of the total.

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THE ROLE OF CATION EXCHANGE IN THE TRANSPORT OF AMMONIUM AND NITRATE IN A SEWAGE-CONTAMINATED AQUIFER

By Marnie L. Ceazan[1], E. Michael Thurman[1],
and Richard L. Smith[1]

Ammonium (NH_4^+) sorption and its effect on transport of ammonium and nitrate has been a focus of research at the Otis Air Force Base (OAB) site, on Cape Cod, Mass. LeBlanc (1984b) found that the plume of sewage-contaminated ground water at the OAB site contains nitrogen in two separate zones, an NH_4^+ containing zone and a nitrate (NO_3^-) containing zone. NH_4^+ is the predominant nitrogen species near the sewage-infiltration beds, but is depleted or absent farther than 1,830 m (meters) from the beds. Conversely, NO_3 is the predominant species of inorganic nitrogen from 1,830 m to the toe of the plume (more than 3,350 m downgradient from the beds). Both NO_3^- and NH_4^+ are present in the modern day sewage effluent; therefore, these results suggest that there is a difference in the relative rates of transport of NH_4^+ and NO_3 within the aquifer. Three geochemical and biological mechanisms which could cause this loss of NH_4^+ are volatilization, nitrification, and sorption. Sorption of NH_4^+ on the aquifer solids is probably the major mechanism of NH_4^+ loss. To test this hypothesis, evidence for sorption was obtained by examination of cation distributions in the sewage plume, and by laboratory and field experiments.

If NH_4^+ sorption is occurring in the sewage plume, then other cations, such as calcium (Ca^{+2}) and magnesium (Mg^{+2}), should be displaced. Field evidence shows this effect, with a Ca^{+2}, Mg^{+2}, and sodium (Na^+) high located downgradient of the NH_4^+ front. Furthermore, potassium (K^+) followed the same general trends as NH_4^+, suggesting the K^+ also sorbed and competes with NH_4^+ for sorption sites. The relative effect of NH_4^+ versus K^+ displacement of Ca^{+2}, Mg^{+2}, and Na^+ is not known.

LABORATORY SORPTION STUDIES

In a laboratory study, extraction of core material collected from the OAB site showed that there was a significant concentration of NH_4^+ sorbed on the aquifer solids. The degree of partitioning of NH_4^+ between the solid and aqueous phases at a given point in the aquifer can be expressed by the distribution coefficient (K_d). The K_d was experimentally determined by means of a laboratory experiment in which dissolved NH_4^+ was allowed to react with core material from the site in a batch reactor. Dissolved NH_4^+ versus sorbed NH_4^+ were plotted to obtain the sorption isotherm, the slope of which is equal to the K_d. As expected theoretically, the isotherm obtained from this experiment was not linear throughout the range of dissolved NH_4^+ concentrations examined; the slope (K_d) decreased as the concentration of sorbed NH_4^+ increased (Grove, 1976). However, the K_d remained constant at about 0.31 mL/cm³ (milliliter per cubic centimeter) of aquifer solids over the dissolved NH_4^+ concentration interval of 1.5 to 20 mg N/L (milligrams of nitrogen per liter).

Using an estimated porosity of 0.38 (LeBlanc and others, in press), and average linear velocity of 0.3 m/d (meters per day) (LeBlanc, 1984a), a bulk density of 1.64 g/cm³ (grams per cubic centimeter), and assuming that the partitioning of the NH_4^+ between the aqueous phase and the solid phase can be

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

adequately described by the K_d of 0.31 mL/cm³ of aquifer material, the retardation of the NH_4^+ front relative to the bulk mass of water can be quantitatively expressed by the following equation:

$$R_f = \bar{v}/\bar{v}_c = 1 + (\rho_b/n)(K_d) \qquad (1)$$

where

$\bar{v}$ = average linear velocity of the ground water,
$\bar{v}_c$ = average linear velocity of the retarded constituent,
K_d = the distribution coefficient,
ρ_b = the bulk density,
n = the porosity, and
R_f = the retardation factor (Freeze and Cherry, 1979).

The $\bar{v}_c$ and R_f calculated from equation 1 are 0.12 m/d and 2.34, respectively. Using these values and assuming a continuous source of NH_4^+ for the 46 years of operation of the OAB sewage treatment plant, the front of the NH_4^+ plume was calculated to be 2,015 m downflow from the contaminant source. This calculated location is similar to the location of the front of the NH_4^+ plume in 1983–85 (about 1,800 m from the disposal site). Hence, the results of these laboratory experiments indicate that retardation of NH_4^+ due to sorption may be very significant at the OAB site.

FIELD TRACER TESTS

Divergent tracer tests were conducted at the OAB site in order to obtain field evidence of NH_4^+ cation exchange. Stephen P. Garabedian (U.S. Geological Survey, Boston, Mass.) designed and coordinated the tracer tests. In these experiments, a radially divergent flow field was formed by continuous injection of native ground water obtained from a nearby well into a well with a 1.4-m-long screen. The injection rate was about 95 L/min (liters per minute). Tracers were added as a pulse into the injection stream and monitored as they moved with the radial flow past a multilevel sampling device located 1.5 m from the injection well. The tracers were monitored at two depths opposite the top and bottom of the injection zone. The tracers included NH_4^+, NO_3^-, K^+, and bromide (Br^-).

Br^- was used as the conservative tracer for these field tests. The arrival times of the peak of the Br^- pulse were different at the two depths (fig. B–17 and fig. B–18). It took three times as long for the Br^- pulse to arrive in the slow zone (top of the injection interval) than the fast zone (bottom of the injection zone). The different transport rates for Br^- are probably due to hydraulic conductivity variations within the aquifer.

The transport of NH_4^+ is significantly retarded in the slow zone, and somewhat retarded in the fast zone (denoted by the tailing of the NH_4^+ peak (fig. B–19 and fig. B–20). The retardation of NH_4^+ was significantly less in the fast zone suggesting that the aquifer has some small-scale stratigraphic variations with differing cation exchange capacities. Conversely, the NO_3^- pulse arrived simultaneously with the injected Br^- pulse in the slow zone (fig. B–21).

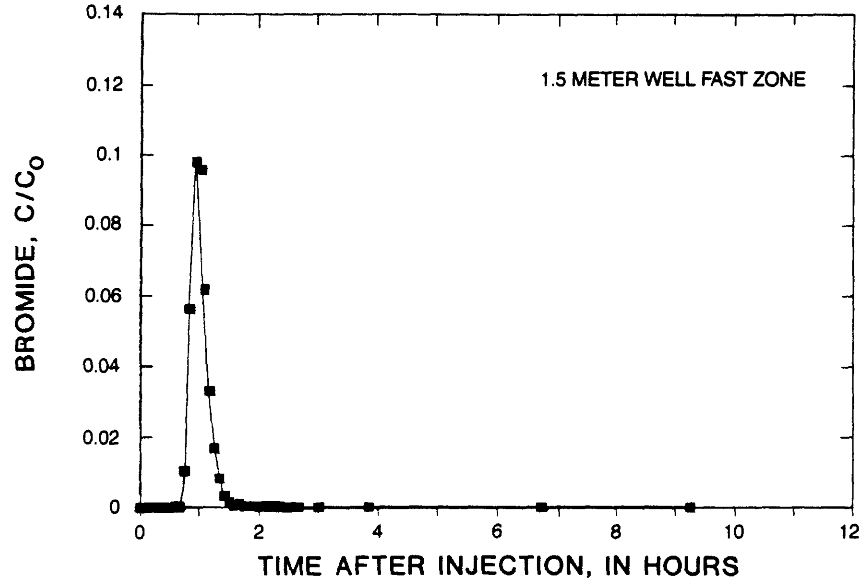

Figure B-17.—The concentration of dissolved bromide divided by concentration of bromide in the injectate versus time, divergent tracer test (fast zone).

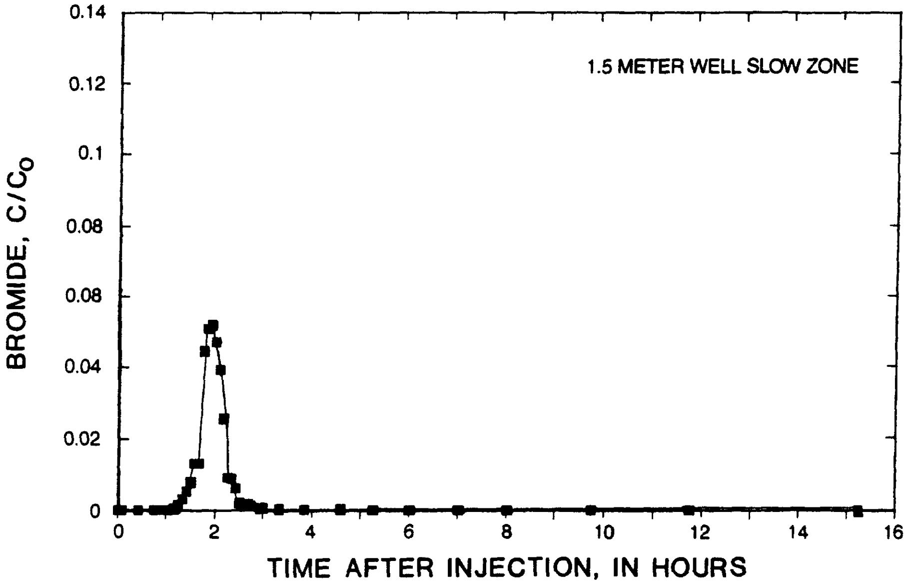

Figure B-18.—The concentration of dissolved bromide divided by concentration of bromide in the injectate versus time, divergent tracer test (slow zone).

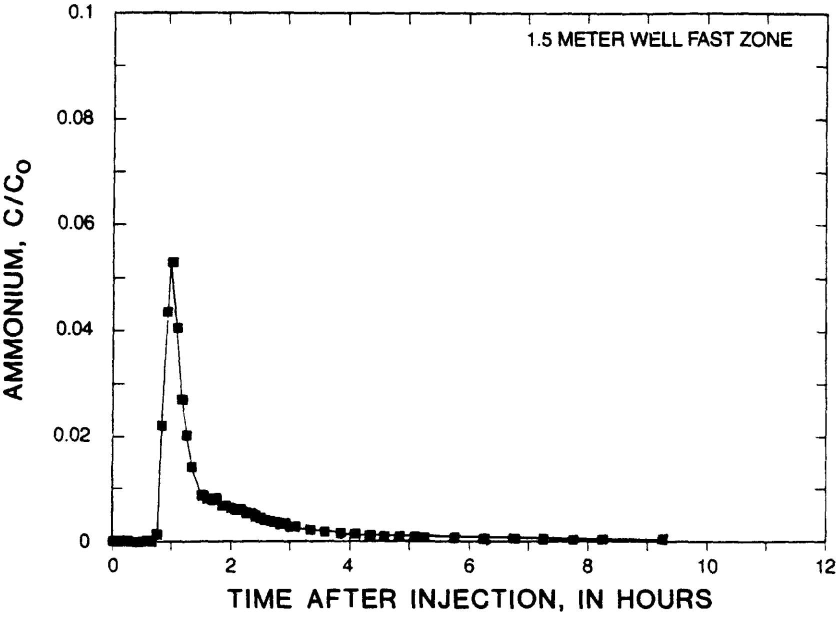

Figure B-19.—The concentration of dissolved ammonium divided by concentration of ammonium in the injectate versus time, divergent tracer test (fast zone).

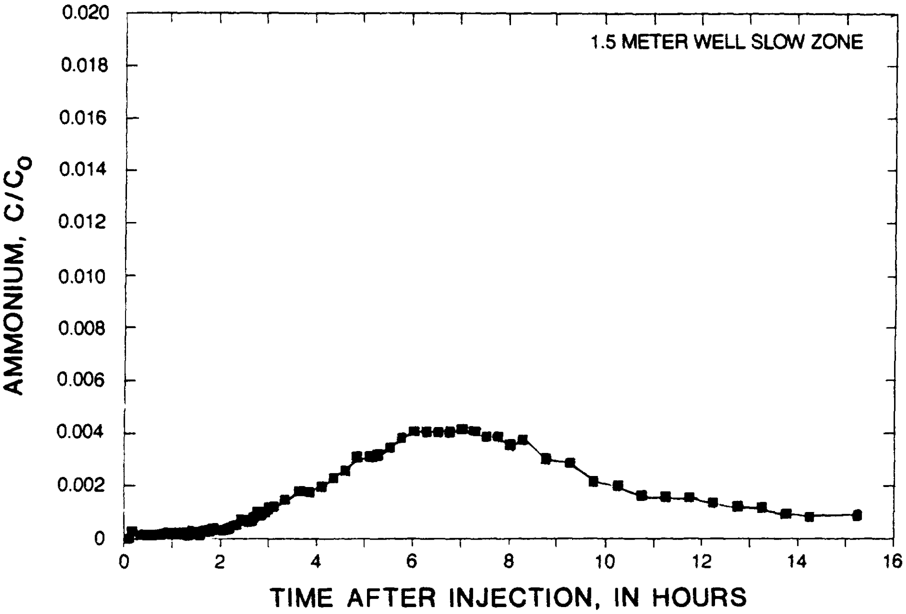

Figure B-20.—The concentration of dissolved ammonium divided by concentration of ammonium in the injectate versus time, divergent tracer test (slow zone).

In the slow zone, where NH_4^+ was retarded, a pulse of Mg^{+2}, Ca^{+2}, Na^+, and K^+ arrived simultaneously with the Br^- pulse (fig. B-22). A second pulse of K^+ was retarded and arrived the same time as the NH_4^+ pulse (fig. B-23). The cause of the two K^+ pulses is unknown.

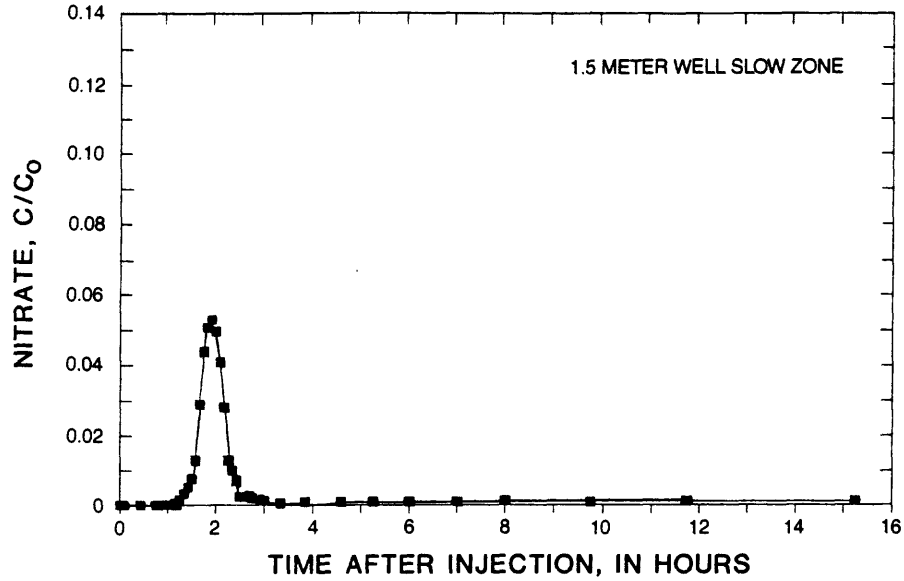

Figure B-21.—The concentration of dissolved nitrate divided by concentration of nitrate in the injectate versus time, divergent tracer test (slow zone).

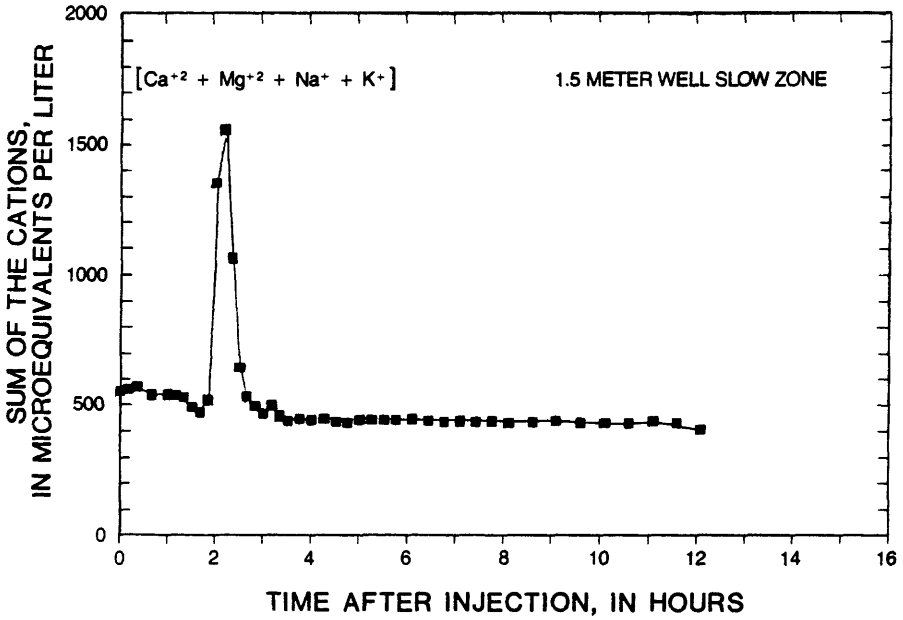

Figure B-22.—The sum of the cations (calcium, magnesium, and sodium) versus time, divergent tracer test (slow zone).

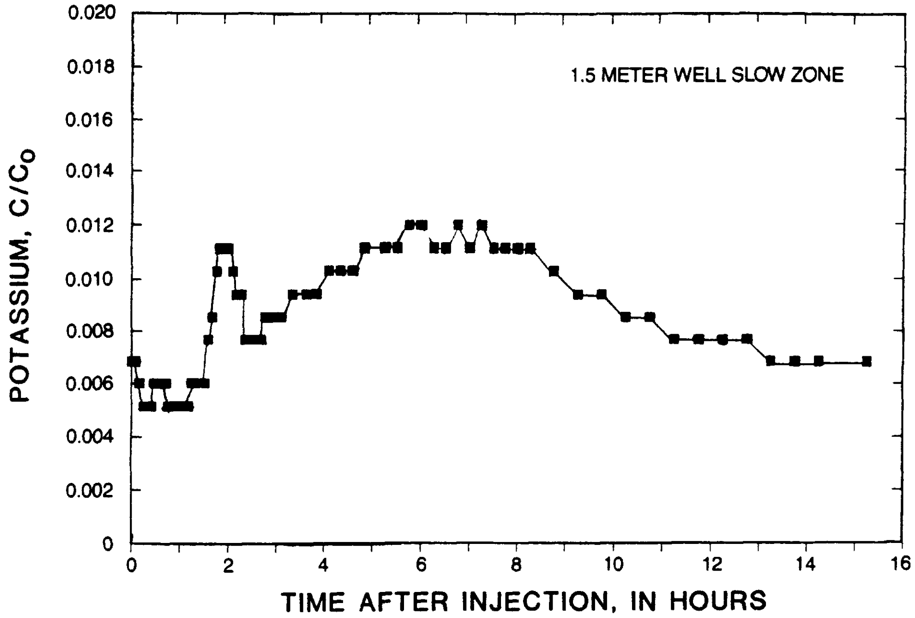

Figure B-23.—The concentration of dissolved potassium divided by concentration of potassium in the injectate versus time, divergent tracer test (slow zone).

The results of the divergent tracer tests show that NH_4^+ and K^+ are retarded relative to the conservative species Br^-, whereas NO_3^- moves conservatively. The NH_4^+ and K^+ displace native cations such as Ca^{+2}, Mg^{+2}, and Na^+ during the exchange process. The test results are consistent with the distributions of these cations in the sewage plume.

In summary, it is evident from laboratory experiments that sorption plays a major role in the retardation of NH_4^+ at the OAB site. There is also strong evidence from contaminant patterns in the sewage plume and from field divergent tracer tests that NH_4^+ and K^+ displace other major cations, causing zones of high Ca^{+2}, Mg^{+2}, and Na^+ downgradient from the NH_4^+ and K^+ contaminant plumes. Field tracer tests also provided evidence that sorption of NH_4^+ was predominantly responsible for transport differences between NH_4^+ and NO_3.

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CHAPTER C.—MOVEMENT AND FATE OF CRUDE OIL CONTAMINANTS IN THE SUBSURFACE ENVIRONMENT AT BEMIDJI, MINNESOTA

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CHAPTER C.—MOVEMENT AND FATE OF CRUDE OIL CONTAMINANTS IN THE SUBSURFACE ENVIRONMENT AT BEMIDJI, MINNESOTA

INTRODUCTION

By Marc F. Hult[1]

On August 20, 1979, a pipeline break in a remote area near Bemidji, Minn. (fig. C-1), resulted in the release of $1.5x10^5$ L (liters) of crude oil. Although about $1.1x10^5$ L were removed from the site as part of the cleanup, some crude oil infiltrated the ground and percolated to the water table. The spill occurred in the recharge area of a local flow system that discharges to a small lake 300 m (meters) downgradient (Hult, 1984).

The aquifer is a pitted and dissected outwash plain underlain at a depth of about 20 m by low-permeability till. Crude oil is floating on the water table about 8 m below land surface and has migrated about 20 m as a separate fluid phase. Soluble petroleum derivatives have dissolved in and are moving with ground water. Volatile constituents are migrating through the unsaturated zone by diffusion.

The abstracts presented in this chapter provide an overview of ongoing efforts to combine the results of interdependent, interdisciplinary research into the comprehensive understanding of the physical, chemical, and biological processes that will be needed to develop predictive models of contaminant mobilization, transport, and fate.

Franzi investigates the relationship between depositional and post-depositional processes and the heterogeneity and anisotropy of the aquifer. Post-depositional subsidence and collapse caused by melting of stagnant ice has created significant geomorphic and hydrogeologic structures. Miller describes a preliminary ground-water flow and chemical-transport model used to assess the effect of these hydrologic discontinuities, estimate aquifer properties, and to guide continuing field work.

Abstracts by Siegel, Bennett, and Berndt describe studies of dissolved inorganic constituents and parameters done to characterize the geochemical environments in and around the site. An anoxic zone, probably plume shaped, extends downgradient of the oil pool and into an oxic zone that surrounds the contamination. Carbonate minerals are actively dissolving in the oxic spray zone upgradient of the oil pool where oil is being mineralized, whereas quartz is dissolving underneath the oil by organic-acid complexation.

Selective leaching experiments show that fractionation of metals is also occurring where the aquifer matrix is contaminated. Morphological analysis of quartz sand grains clearly show unusual rock-water interactions are occurring in the anaerobic contaminant zone. Preliminary analysis indicates the possibility of an organic/quartz interaction that is significantly increasing the mobility of silica through the system.

Predictions of the evolution and ultimate geometry of contaminant plumes resulting from spills require quantitative descriptions of the rate of mass transfer from the organic fluid to ground water. Pfannkuch presents laboratory and field work that describe how the the rate of oil dissolution, and therefore the strength of the contaminant source, is controlled by fluctuations in ground-water velocity and water-table fluctuations.

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[1] U.S. Geological Survey, St. Paul, Minn.

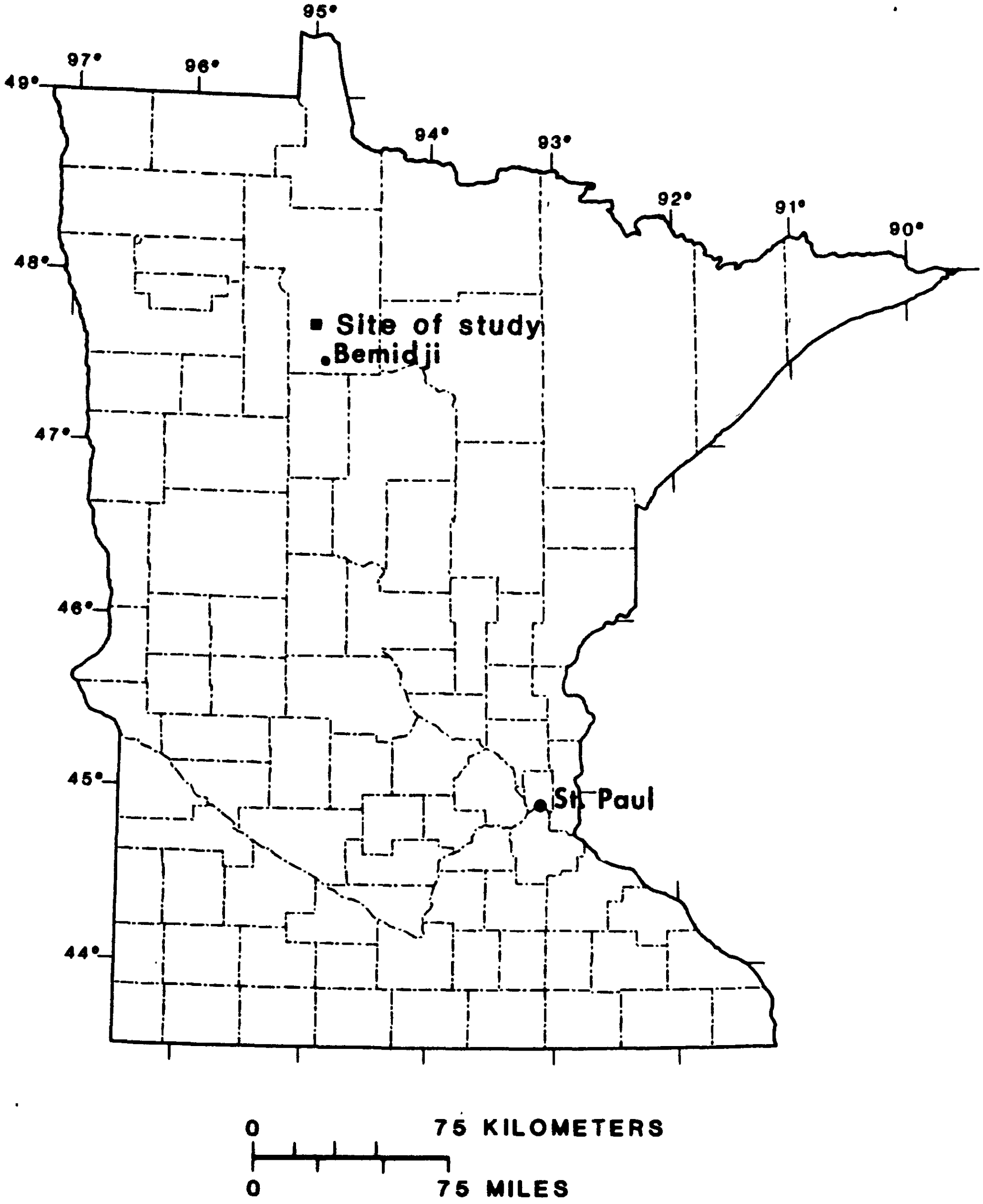

Figure C-1.—Location of Bemidji, Minnesota, study site.

Baedecker and others present an overview of the distribution of organic substances in the system and evidence for strong attenuation of the organics in the dissolved plume by volatilization, biodegradation, dilution, and(or) sorption. In the anoxic part of the plume, volatile organic acids are present that are intermediate degradation products of the original oil. Hydrocarbons in the original oil with more than about 10 carbon atoms seem to be very immobile owing to their low aqueous solubilty and tendency to sorb on the sediments.

Hult presents a model for the mobilization, transport, and fate of volatile hydrocarbons in the unsaturated zone which accounts for a major part of the organic carbon moving through the subsurface. The distribution and concentrations of carbon dioxide, oxygen, and hydrocarbons are in good stoichiometric agreement with the conclusion that hydrocarbon vapors are mineralized to carbon dioxide and water by bacteria where the partial pressure of oxygen is sufficient for aerobic metabolism. Hydrocarbons are degraded to methane, carbon dioxide, and, possibly, hydrogen where the oxygen has been depleted. Baehr and Hult present preliminary approaches to quantitative modeling of the diffusion and oxidation hydrocarbon vapors.

Eganhouse and others describe the transport and fate of monoaromatic hydrocarbons such as benzene, toulene, and xylenes. Of the original constituents of the petroleum, this is the class of compounds that is the most mobile in the aqueous environment. Distinct compositional changes are noted that are attributed to differences in the rate of degradation of individual compounds.

Aiken and Thorn isolated non-volatile organic acids which account for about 70 percent of the dissolved organic carbon in the plume. Preliminary GC-MS and NMR analyses indicate that the compounds include a complex mixture of intermediate metabolites from microbial degradation of the oil.

Rees and Ranville present an assessment of the role of colloids in the transport of organic matter. Preliminary field work identified a variety of inorganic colloids, and possibly stable microemulsions and(or) micellar aggregates which may be mobile and serve to move hydrophobic constituents.

Chang and others correlate the biomass of hydrocarbon-degrading bacteria with adenosine triphosphate concentrations in sediment samples. Additionally, the sensitivity of the rate of hydrocarbon degradation to environmental factors such as oxygen and nutrient availabilty and temperature were determined in laboratory experiments.

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SEDIMENTARY AND POST-DEPOSITIONAL PROCESSES RELATED TO AQUIFER PROPERTIES AT THE BEMIDJI RESEARCH SITE, NORTH-CENTRAL MINNESOTA

By D. A. Franzi[1]

The Bemidji research site is located on a pitted and regionally dissected outwash plain that is bordered on the north by a moraine complex and on the south and west by a low-relief, till-veneered upland. Four glacial lithofacies associations, each of which contains a diamicton unit and genetically related stratified deposits, are recognized on the basis of well-log data and surface morphostratigraphic relationships. The diamictons provide an important basis for subsurface lithofacies correlations since they are easily recognized on the basis of texture, composition, and physical properties. Erosional contacts and intercalation of lacustrine sediment indicate that each lithofacies association represents a separate phase of late-glacial sedimentation. The subsurface distribution of the materials suggests that the deposits, landforms, and stagnant ice left after each glacial phase, affected the depositional environments of subsequent phases. The result is a highly complex assemblage of drift units of different ages that can be predicted only in general terms. The units have been modified to varying degrees by secondary processes related to the formation of kettles.

The surficial aquifer is composed of ice-contact stratified drift and outwash that range in texture from moderately well sorted to poorly sorted sand. Estimates of intrinsic permeability based on the grain-size characteristics of the aquifer materials range from $1.0\text{x}10^{-7}$ to $1.0\text{x}10^{-6}$ cm^2 (square centimeters). Discontinuous bodies of till, sediment-flow deposits, and lacustrine silt and clay form semiconfining layers that are distributed sporadically throughout the sedimentary sequence. A regionally extensive till layer, at depths of 23 to 31 m (meters) near the spill site, forms the base of the surficial aquifer. The upper part of the aquifer consists of 7 to 20 m of outwash sand and gravelly sand. Stratigraphic evidence indicates that the ice that deposited the outwash terminated against the northern flank of the moraine complex and spread into the Clearwater River Valley to a position marked by a head of outwash approximately 2 kilometers northwest of the study site. The extensively pitted surface of the outwash, even beyond the projected margin of the ice front, indicates that the material was deposited over older glacial sediment that contained significant amounts of stagnant ice.

The hydrologic characteristics of the outwash are the result of its depositional environment and secondary subsidence and collapse related to the formation of kettles. Stratigraphic reconstructions from surface morphological relationships, test drilling, and ground-penetrating-radar surveys indicate that kettle development occurrred before, during, and after outwash deposition. An important effect of this process is the development of locally thick accumulations of coarse-grained outwash associated with high-angle faults and zones of disrupted bedding. Small bodies of fine-grained sediment within the outwash sequence may represent overbank deposits or represent local accumulations in abandoned channels or isolated kettle depressions.

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[1] State University of New York, Plattsburgh, N.Y.

EFFECTS OF LOCAL HYDRAULIC DISCONTINUITIES ON THE TRANSPORT OF CRUDE-OIL RESIDUALS IN GROUND WATER, BEMIDJI, MINNESOTA, RESEARCH SITE

By Robert T. Miller[1]

A local, two-dimensional, cross-sectional, ground-water-flow and contaminant-transport model was constructed along an assumed ground-water-flow path at the site of a crude-oil spill, near Bemidji, Minn. The cross-sectional model was used to evaluate the effects of large hydraulic discontinuities in the flow field on transport of crude-oil residuals and to aid in selection of vertical chemical-quality-sampling locations along the flow path downgradient from the spill site.

Analysis of core samples from mud-rotary drilling and preliminary interpretation of ground-penetrating-radar data suggest the possibility of large discontinuities in the hydraulic characteristics of unconsolidated materials at the spill site due to secondary subsidence and collapse related to the formation of kettles (Franzi and others, 1987). The local cross-sectional model is a refinement of preliminary models used to evaluate the potential regional effects on contaminant movement of changes in recharge, lake levels, and regional variations in hydraulic characteristics of the aquifer.

The local cross-sectional model simulates a saturated area 200 m (meters) long by 6 m deep. The model uses finite-difference techniques to solve the coupled equations of ground-water flow and contaminant transport. Model discretization is uniform in both the horizontal and vertical directions with 5.0 m and 0.15 m node spacings, respectively.

The hydrogeologic complexities simulated with the local cross-sectional model ranged from fully isotropic and homogeneous with horizontal flow to anisotropic, nonhomogeneous horizontal layers that are 0.15 m thick and may contain a vertical-flow component. Secondary subsidence and collapse features in the aquifer were simulated as abrupt changes in aquifer characteristics in the horizontal direction. All model simulations were for a period of 7 years, and assume that the crude-oil residuals have no effect on viscosity and density of the ground water.

Horizontal intrinsic permeabilities and porosities simulated with the model ranged from 4.0×10^{-12} to 27.5×10^{-12} square meters and 25 to 40 percent, respectively. The maximum ratio of horizontal to vertical permeability simulated is 10:1. Model simulations for the case of a homogeneous, isotropic aquifer suggest that after 7 years of transport a 10-percent-mass fraction of a conservative constituent might move vertically to a depth of 5 m below the water table and horizontally 170 m downgradient from the crude-oil source. Other, more complex, simulations of the aquifer system indicate that vertical migration of crude-oil residuals may be influenced by secondary subsidence-collapse features and a buried, high-permeability esker beneath the spill site.

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[1] U.S. Geological Survey, St. Paul, Minn.

BULK AND DISTRIBUTED PARAMETER MASS-TRANSFER MODELS FOR DETERMINATION OF THE SOURCE STRENGTH AT AN OIL SPILL/GROUND-WATER INTERFACE

By Hans-Olaf Pfannkuch[1]

Determination of the mass-transfer rate (dissolution) of hydrocarbons across a hydrocarbon spill/ground-water interface is essential for modeling dissolved contaminant plume development in ground water. The source strength varies spatially and may vary with time because of changing environmental conditions. The variation of source strength controls the internal structure of the plume, its maximum extent, and the length of time the plume will persist in the environment.

A first approximation of the mass-transfer coefficient was obtained from bulk mass-transfer experiments in columns for pure alkanes (pentane, hexane, and heptane). Theory and experimental data from literature suggest the mass-transfer coefficient is independent of velocity for low Peclet numbers. However, the measured coefficient was dependent on velocity for Peclet numbers greater than one. The small grain sizes needed to generate low Peclet numbers (0.5 millimeter) created a capillary fringe between the alkane and water which could not be suppressed. Representative results are shown in table C-1. Average pore velocities of $0.1\text{x}10^{-5}$ to $1.0\text{x}10^{-5}$ meters per second used in the columns correspond to representative values of ground-water velocities (0.1–1.0 meter per day) at the Bemidji, Minn., research site. The mass transfer coefficient values from 0.1 to 1,000 micrograms per square meter per second fall within the range of values given in the literature.

Mass transfer increased when water-table fluctuations were simulated because the non-wetting phase dispersed into separate globules within the zone of fluctuation increasing the effective contact area. As shown in table C-1 for two experiments with heptane, the mass-transfer coefficient increases as the fluctuation amplitude increases.

A two-dimensional model was derived to describe the development of the dissolved contaminant plume under an oil body. The assumptions are: (1) the oil body is immobile, (2) the water velocity at the oil-body surface is zero, and (3) no other degradation processes occur such as microbial activity, or change in redox potential or pH.

The mass transfer of hydrocarbons across the oil body/water interface depends upon: (1) the concentration of the hydrocarbon in the water, (2) the solubility of the hydrocarbon in water, and (3) time, because the concentrations and solubilities may change with time. In multicomponent systems the mass transfer also depends upon the mole fraction distribution of the components. Also, components with low solubilities may form a rind at the interface which is a barrier to the more soluble components in the oil body.

In a system in which the water is stagnant the concentration profile of dissolved hydrocarbons would be downward, and would be independent of position along the oil body but dependent on the molecular diffusion coefficient. In a ground-water flow system the diffusion of hydrocarbons into the water is due to mass transfer at the leading edge of the oil body. A contaminant plume evolves downstream until, theoretically, the advected hydrocarbon concentration reaches equilibrium. Further downgradient, mass transfer (dissolution) of the hydrocarbon from the oil body ceases. The purpose of modeling is to

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[1] University of Minnesota, Minneapolis, Minn.

determine the flow parameters and conditions that control this active exchange zone, its migration when the components of interest are leached out of the oil body, and the critical conditions under which these zones will be established.

Table C-1.—*Experimentally determined mass-transfer coefficients for pentane, hexane, and heptane*

[mm, millimeter; m/s, meter per second; (μg/m^2)/s, microgram per square meter per second]

Compound	Grain size, mm	Average pore velocity, (m/s)x10^5	Mass-transfer coefficient, (μg/m^2)/s
Pentane	0.5	5.5	31.00
		13.9	106.92
		83.7	543.84
		178.0	1,430.96
Hexane	.5	.144	.15
		4.34	2.29
		5.32	4.25
		17.5	12.85
		79.02	28.88
		233.2	147.97
Heptane	.25	.153	.02
		.681	.28
		1.73	.83
		16.23	3.14
Heptane	.5	2.18	.63
		5.08	1.40
		16.42	4.31
		133.9	24.81
Heptane[1]	.5	5.61	2.60
		71.4	33.83
Heptane[2]	.5	7.12	6.49
		11.2	5.56
		16.7	7.38
		32.4	31.34
		66.07	46.42

[1] Water table fluctuated about 1 centimeter.

[2] Water table fluctuated across entire column width.

Because the zone of active exchange forms at or near the upstream end of the oil body, the upstream end of the oil body should show an increase in viscosity and density compared to the downstream end because of the loss of the more volatile and soluble components. Samples from the free oil phase of the two oil pools at the Bemidji, Minn., research site show that the viscosity and density increase from downstream to upstream in the oil pools. However, some of the wells sampled are located in areas where the oil spill was excavated and the oil may have been exposed to air for differing times.

GEOCHEMICAL FACIES AND MINERAL DISSOLUTION
BEMIDJI, MINNESOTA, RESEARCH SITE

By Donald I. Siegel[1]

This paper presents a generalized model for reactions between aqueous and solid phases at the Bemidji, Minn., research site based on results from the first year of study (Siegel and others, 1986; 1987) and additional sampling and laboratory studies completed in 1986. Samples of ground water were collected in July 1986 from all wells downgradient and at selected wells upgradient from the oil body and analyzed for pH, Eh, dissolved oxygen, major solutes, and selected trace metals. Details of the solid-phase studies are found in Berndt (Chapter C, this report) and Bennett (Chapter C, this report).

Four geochemical zones are defined by differences in Eh, pH, and concentrations of dissolved solutes (fig. C–2a). Background ground water of calcium-magnesium-bicarbonate type has dissolved-solids concentrations less than 400 mg/L (milligrams per liter), measurable dissolved oxygen, and dissolved iron and manganese concentrations less than 0.1 mg/L. This oxic background zone grades into the oxic spray zone upgradient of the floating oil body. Within this oxic spray zone (fig. C–2b), carbonate minerals (and perhaps aluminosilicate minerals) in the aquifer matrix are dissolving. The maximum concentration of dissolved solids (greater than 1,200 mg/L) occurs in this zone. The increase in dissolved solids is caused almost entirely by increases in concentrations of bicarbonate and alkaline earths released by carbonate dissolution. Carbonate dissolution in this zone may be caused by elevated concentrations of carbonic and organic acids produced during bacterial oxidation of the oil in the unsaturated zone of the spray zone. In the spray zone, as well as downgradient from the oil body, the overall water type (calcium-magnesium-bicarbonate) remains the same. Ground water is in equilibrium with calcite, undersaturated with respect to dolomite, and supersaturated with respect to quartz.

The aquifer matrix within the oil body is relatively nonreactive because the sediment grains are coated with oil (Bennett and Siegel, 1987). An anoxic zone (fig. C–2c) occurs directly under the oil and extends downgradient in a plume characterized by negligible dissolved oxygen, concentrations of dissolved organic carbon over 20 mg/L, and negative to slightly positive Eh. In the part of the plume that is most reduced, iron concentrations exceed 50 mg/L. Within this anoxic zone, marked dissolution of quartz occurs, probably because of the formation of silica-organic acid complexes (Bennett, Chapter C, this report). Silica concentrations are as much as 10 times the equilibrium concentration of quartz (Bennett, Chapter C, this report; Bennett and Siegel, 1987). Maximum concentrations of aluminum also occur in the anoxic zone, but farther downgradient from where the quartz is being dissolved. The higher concentrations of aluminum may be related to dissolution of aluminosilicate minerals coupled with aluminum-forming complexes with organic acid. Because of carbon dioxide degassing, carbonate minerals precipitate in the anoxic zone and in an oxic zone surrounding it. This downgradient oxic zone is characterized by detectable dissolved oxygen, negligible concentrations of iron, and positive Eh. In this zone, carbonate minerals precipitate because of the degassing of carbon dioxide, whereas iron and silica probably precipitate because of the oxidation of ferrous iron and silica-organic acid complexes, respectively. Solid-phase evidence for these precipitation processes are found in Bennett (Chapter C, this report) and Berndt (Chapter C, this report).

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[1] Syracuse University, Syracuse, N.Y.

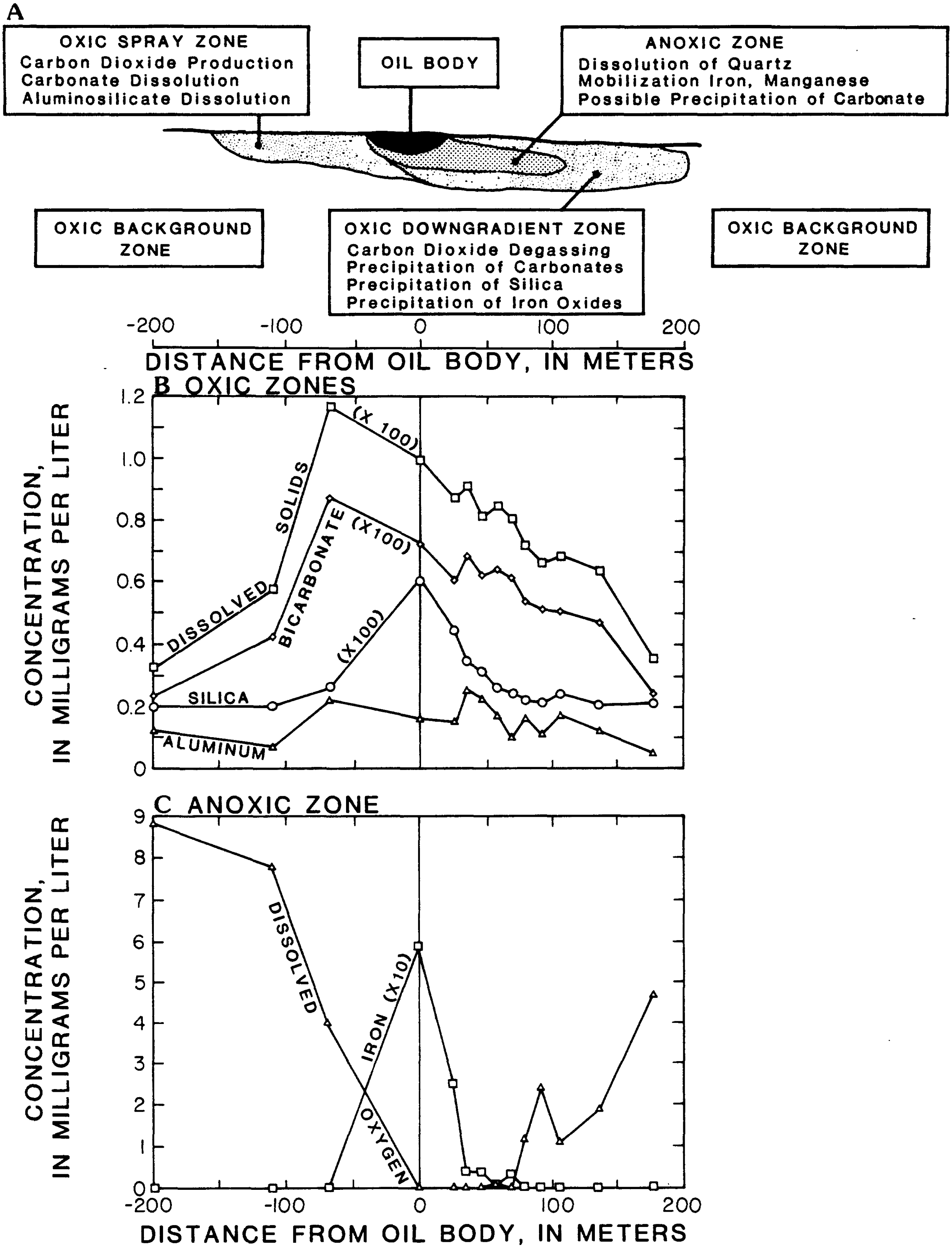

Figure C-2.—Geochemical facies and trends.

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METAL PARTITIONING IN AQUIFER SEDIMENTS, BEMIDJI, MINNESOTA, RESEARCH SITE

By Marian P. Berndt[1]

Ground-water chemistry near an oil body at the research site suggests the transfer of major and trace metals between the aqueous and solid phases. Whole-rock chemistry and metal partitioning of the aquifer sediments were studied to identify processes that affect the transfer of metals from the aqueous to the solid phase downgradient from the oil. Two size fractions of sediments were analyzed: 2 to 4 phi (62-250 micrometers) and greater than 4 phi (less than 62 micrometers). The two fractions showed similar distribution of metals, but the greater-than-4-phi fraction contained much higher concentrations of the metals of interest, so only results from study of this fraction are presented here.

The bulk chemistry of the aquifer sediments was determined using direct current plasma spectrometry (Feigenson and Carr, 1985) on samples collected along the axis of the contaminant plume downgradient from the oil body. Most of the metal-oxide percentages varied little along the axis of the plume (table C-2). However, calcium oxide increased from 7.8 percent in the sample closest to the oil body to 17 percent at 68 meters downgradient from the oil body.

Table C-2.—*Composition of sediment size fraction greater than 4 phi*

[Values are in percentage of composition unless otherwise noted]

Oxide	Distance from the center of the oil body, in meters					Background
	24	35	46	68	91	
Silicon dioxide, SiO_2	53	51	52	48	55	56
Calcium oxide, CaO	7.8	14	15	17	11	11
Iron oxide, Fe_2O_3	4.0	7.6	4.0	4.5	4.7	3.0
Magnesium oxide, MgO	4.3	5.0	5.7	6.5	4.4	4.9
Aluminum oxide, Al_2O_3	7.5	7.3	7.9	6.9	8.8	7.6
Sodium oxide, Na_2O	1.7	1.9	1.8	1.7	1.9	2.0
Potassium oxide, K_2O	1.1	1.1	1.2	1.0	1.3	1.4
Manganese oxide, MnO	.07	.08	.08	.07	.09	.07
Strontium[1], Sr	250	250	250	230	240	280
Vanadium[1], V	80	90	80	90	100	90

[1] Values are in ppm (parts per million).

A selective extraction procedure modified from Filipek and others (1981) was used to determine the partitioning of metals in the following phases: (1) exchangeable or bound to carbonates, (2) in hydrous manganese-oxides, (3) complexed with organic matter, (4) in hydrous iron-oxides, and (5) in the residual crystalline fraction. The extractions show that calcium concentrations in the carbonate fraction increase with distance downgradient from the oil, similar to that of total calcium in the whole-rock chemistry

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[1] Syracuse University, Syracuse, N.Y.

(shown as total calcium for comparison to carbonate calcium in fig. C-3). This trend in calcium concentration indicates carbonate precipitation and agrees with the ground-water chemistry along the plume. Calcite is everywhere at equilibrium with ground water, and precipitation of calcite might occur as the partial pressure of carbon dioxide decreases from $10^{-0.96}$ atmospheres under the oil to $10^{-1.3}$ downgradient from the oil (fig. C-4).

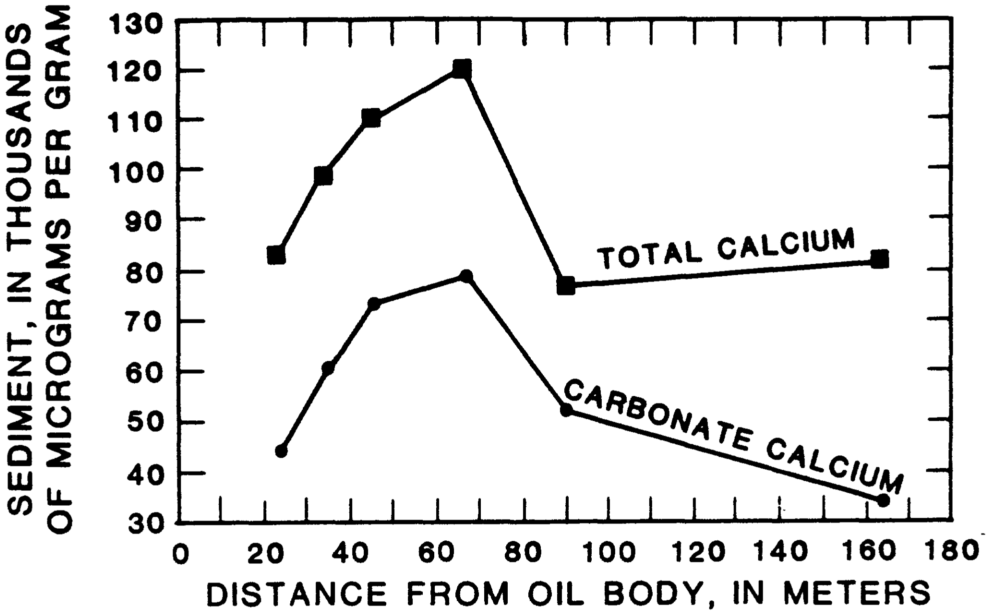

Figure C-3.—Trends of total calcium and carbonate calcium versus distance from the oil body.

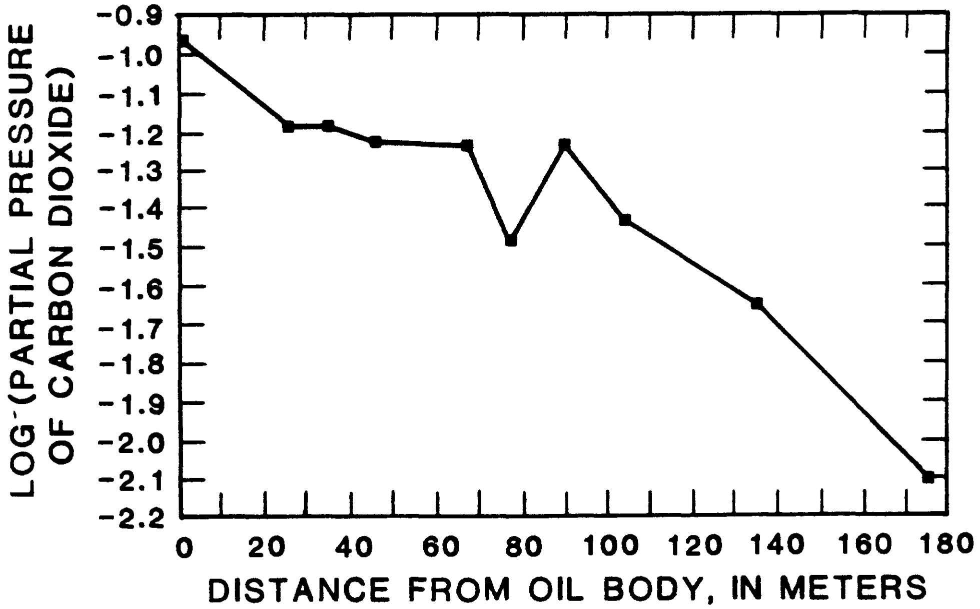

Figure C-4.—Logarithm of the partial pressure of carbon dioxide versus the distance from the oil body.

The majority of the total iron in all sediment samples was complexed with organic matter (25–48 percent) and in the residual fraction (48–73 percent). No systematic variation in iron partitioning was noted along the plume axis, although changes in the concentration of dissolved oxygen and dissolved iron in the ground water indicate transfer of iron from the aqueous to the solid phase (Siegel, Chapter C, this report). This lack of increase of iron in the sediments probably results from sediment samples not being collected in or beneath the oil body where changes in the geochemistry of iron are occurring.

Manganese was predominantly in the carbonate fraction (42–58 percent), with smaller quantities complexed with organic matter (9–16 percent) and in hydrous manganese-oxides (1–20 percent). Total strontium and vanadium concentrations are very low in the sediments (table C–2). The residual fraction contained the largest amount of strontium (72–83 percent), with small amounts in the carbonate fraction (17–28 percent). Similarly, the highest concentrations of vanadium were in the residual fraction (53–73 percent), with small amounts in the carbonate fraction (17–29 percent) and complexed with organic matter (11–22 percent).

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SOLID PHASE STUDIES OF AQUIFER SEDIMENTS, BEMIDJI, MINNESOTA, RESEARCH SITE

By Philip C. Bennett[1]

Analyses of dissolved inorganic constituents in the contaminated zone at the Bemidji, Minn., research site show that significant rock-water interaction is occurring in response to organic contamination. Dominant geochemical processes were determined from the general mineralogy, bulk-mineral chemistry, and surface morphologies of individual grains of sediment collected from the water table at the site. Laboratory experiments were used to investigate a novel organic/silica interaction identified at the site.

Sediment samples were collected from wells along the axis of the plume of contaminated water and from within the oil body itself. The mineralogy of the size fraction between 2 and 4 phi (65 and 250 micrometer) was determined by both standard optical petrographic methods and an automated scanning electron microscope (SEM) method. An average of all sampling points is shown in table C-3.

Table C-3.—*Sediment mineralogy by optical and scanning electron microscope (SEM) point-count methods, in percent*

Method	Quartz	Plagioclase feldspar	Alkali feldspar	Carbonate	Hornblende	Other
Optical	53	21	14	6.3	2.0	4.2
SEM	57	18	11	5.2	2.2	6.3

The two methods offer comparable results. However, the SEM method is faster and better identifies weathered, opaque minerals. The relative mineral abundances do not differ significantly between sampling points along the plume.

Whole-rock chemistry of the size fraction between 2 and 4 phi was determined using a direct current plasma spectrometer. Results are summarized in table C-4.

Table C-4.—*Bulk elemental analysis in oxide percent, 2 to 4 phi fraction*

Oxide	Distance from oil center, in meters 24	35	46	68	Background
Silica dioxide, SiO_2	72	75	74	75	75
Calcium oxide, CaO	4.7	4.5	4.5	3.5	3.7
Magnesium oxide, MgO	1.0	1.0	1.0	.6	.7
Iron oxide, Fe_2O_3	2.1	2.2	2.1	1.5	1.5
Aluminum oxide, Al_2O_3	7.3	7.9	7.5	7.6	7.6
Sodium oxide, Na_2O	2.2	2.2	2.2	2.2	2.2
Potassium oxide, K_2O	1.2	1.4	1.4	1.3	1.4

The bulk chemistry is fairly consistent down the plume axis. Trends seen in iron-oxide percentages, which are elevated at sites closest to the oil pool, indicate possible precipitation of an unknown iron phase.

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[1] Syracuse University, Syracuse, N.Y.

The surface features of individual sand grains from each sampling site were examined using SEM. Quartz grains from uncontaminated background locations have surface features typical of recent glacial origin. Grain surfaces have highly angular outlines and smooth conchoidal fractures produced by mechanical crushing (Krinsley and Doornkamp, 1973). Evidence of short-range fluvial transport is seen on some grain surfaces as typified by V-shaped impact pits. Grains from within the oil body showed surface features identical to the background samples.

Quartz grains from sampling points immediately downgradient from the oil body show clear evidence of rapid chemical weathering. Triangular etch pits, solution channels, and pitted surfaces indicate a degree of chemical weathering usually seen only in tropical soil zones or in laboratory reactions with hydrofluoric acid. The etching is greatest where the concentration of dissolved organic carbon (DOC) in ground water is highest, and decreases rapidly downgradient. No etching is seen on quartz grains farther than 40 m (meters) downgradient of the center of the oil body. Aluminosilicate grain surfaces show similar trends along the plume axis.

Precipitation of silica occurs on quartz grains 30 to 50 m downgradient from the oil body. The precipitate occurs both as amorphous silica and authigenic quartz. The zone of precipitation is apparently very narrow, extending over less than 30 m of the contaminant plume. At distances greater than 150 m from the oil body, all sand grains display essentially background surface morphologies.

The grain-surface analysis indicates a significant interaction between DOC generated from the degradation of oil and the solid silicate phases. Dissolution of quartz occurs in waters containing 10 to 15 times the equilibrium concentration of dissolved silica and at neutral pH. Not only is the solubility apparently higher in the organic-rich waters, but the etching of the grains indicates a more rapid rate of dissolution as well.

Simple dissolution experiments were done with quartz powders to investigate the potential of organic acids to interact with silica. Preliminary results of these experiments show that some dilute organic acids dissolve quartz far more rapidly than pure water at neutral pH. Mass transfer of silica into solution was 10 times faster in 10 millimolar citrate solution compared to the same quartz powder in distilled water. However, mass transfer of silica in a citric acid solution at pH 2.3 was only slightly above that of water.

The results of this study show that significant rock-water interactions occur in response to elevated concentrations of DOC. Bulk sediment chemistry shows a trend in carbonate and iron oxides along the plume axis. Quartz and aluminosilicate grain-surface morphologies show rapid dissolution of the solid phase where concentrations of DOC are greatest (Bennett and Siegel, in press). Preliminary laboratory investigation of a silica/organic interaction indicates a significant mobilization of silica from quartz by citric acid at neutral pH. Plans are for future studies to focus on the organic acid complexation of silica.

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THE COMPOSITION AND FATE OF HYDROCARBONS IN A SHALLOW GLACIAL-OUTWASH AQUIFER

By M. J. Baedecker[1], I. M. Cozzarelli[1], and J. A. Hopple[1]

Crude oil at the water table of a shallow aquifer in glacial outwash near Bemidji, Minn., has resulted in a contaminant plume downgradient of the oil body. The oil spill occurred about 7 years ago and the flow rate of ground water in the aquifer is about 0.3 to 1.2 m/d (meters per day) (Hult, 1984). The concentration of dissolved organic carbon (DOC) in ground water close to the source is 50 mg/L (milligrams per liter), of which about 30 percent is volatile organic carbon. Concentrations of DOC are 4.2 mg/L at 180 m (meters) downgradient of the oil body, and trace amounts of volatile organic compounds are detectable (Eganhouse and others, Chapter C, this report). The presence of only trace quantities of hydrocarbons beyond 180 m from the source indicates that they are attenuated. The possible processes include volatilization, biodegradation, water-washing, sorption, and dilution.

An anoxic plume has developed under the oil and extends 90 m downgradient. This thin anoxic plume extends vertically from the water-table surface to a depth of 4 m below the water table at its midpoint. The plume is characterized by the absence of oxygen and the presence of methane, ferrous iron, and trace quantities of sulfide. In addition, volatile organic acids generated by anaerobic processes associated with the degradation of organic material are present in the plume.

Several types of acids and the alcohol, phenol, are found in water as analyzed by an ether-extraction technique. The concentrations of volatile acids (expressed as mg/L carbon for compounds C_2 to C_9) in water close to the water-table surface are about 2.1 mg/L at 26 m from the source, 2.3 mg/L at 36 m from the source, and 0.3 mg/L at 90 m from the source. The highest concentrations of acids are immediately downgradient of the oil body in the anoxic plume. Acetic acid is the predominant aliphatic monocarboxylic acid and its concentration is between 20 and 130 μg/L (micrograms per liter) in the anoxic plume. Other acids identified are benzoic, 2-methylbenzoic, 4-methylbenzoic, 2,4,5-trimethylbenzoic, 2,4,6-trimethylbenzoic, cyclohexanoic, and dimethylcyclohexanoic acid. Pyruvic and lactic acids were tentatively identified. These latter two acids are rapidly utilized by micro-organisms and have not been identified previously in ground water.

Although higher molecular-weight hydrocarbons (greater than C_{10}) from crude oil are found in water only where the water is in contact with sediment containing oil or an oil film, these hydrocarbons are found on sediment further downgradient. Hydrocarbons (C_{10}–C_{36} range) in sediment at the water table are predominantly normal hydrocarbons. Their concentrations decrease rapidly away from the source and their distribution indicates that components of lighter molecular weight are preferentially removed, probably by volatilization. Within 65 m of the source, the concentrations of hydrocarbons in sediment decrease by a factor of 10^3 to levels of naturally occurring hydrocarbons (100 nanograms per gram sediment).

The fate and movement of hydrocarbons in a shallow aquifer are controlled by several reactions and processes. The solubilities and volatilities of specific compounds are properties that determine their movement in the

[1] U.S. Geological Survey, Reston, Va.

aquifer. Hydrocarbons of higher molecular weight that are insoluble are sorbed on the sediment. The selective removal of hydrocarbons and the presence of products from microbial processes indicate that degradation is a major mechanism for the attenuation of hydrocarbons.

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MICROBIAL OXIDATION OF PETROLEUM VAPORS IN THE UNSATURATED ZONE

By M. F. Hult[1]

The long-term fate of many organic ground-water contaminants is controlled by microbially mediated oxidation. Conversion to carbon dioxide of petroleum-derived vapors in the unsaturated zone has been documented at a research site near Bemidji, Minn. Crude oil spilled in 1979 is floating on the water table about 8 m (meters) below land surface in a glacial outwash aquifer. The oil is dissolving in the moving ground water and vaporizing into the unsaturated zone. The oil is becoming denser, more viscous, and depleted in compounds with low molecular weights. Aromatic compounds preferentially dissolve in the ground water while alkanes of comparable molecular weight partion to the soil gas.

Gas samples were collected from: (1) permanently installed sampling tubes made of 0.6-cm (centimeter) diameter stainless steel and completed at various depths below land surface, (2) a probe made from 2.9-cm diameter drill rod and wire-wound screen that was driven through the unsaturated zone, (3) the headspace of cores and fluid samples, and (4) from 5-cm diameter test wells that are screened through the water table and, therefore, yield gas from the unsaturated zone. Samples were analyzed in a mobile laboratory immediately after collection using multiple-column gas chromatography and flame-ionization, photo-ionization, and thermal-conductivity detectors to determine the concentration of methane, major aliphatic and aromatic hydrocarbons, oxygen, carbon dioxide, and nitrogen.

Oxygen is diffusing downward from land surface and is used by microbes in the unsaturated zone to oxidize volatile hydrocarbons that are diffusing upward from the oil and contaminated ground water. The partial pressure of oxygen decreases from 0.21 both near land surface and at the water table 70 m downgradient from the floating oil, to less than 0.01 immediately above the floating oil. The partial pressure of oxygen near the water table at the edge of the floating oil is about 0.16, suggesting that the rate of oxygen diffusion through the unsaturated zone is not limiting microbial oxidation of oil components dissolved in the ground water. The decrease in oxygen is paralleled by an increase in the partial pressure of carbon dioxide from 0.0003 to 0.15. Mass-balance calculations and water analyses indicate that the carbon dioxide is being produced in both the unsaturated and saturated zones. In an anaerobic region above the oil, the methane concentration exceeds 8,000 milligrams per liter by volume. The methane is apparently being produced by reduction of intermediate degradation products in both the saturated and unsaturated zones.

Analysis of soil gases has been used as a reconnaissance technique in evaluating specific problems and for monitoring sites of potential leaks, such as at underground storage tanks, because gas analyses can be done conveniently in the field using conventional chromatographic methods, portable instruments, and(or) compound-specific sensors. The areal distribution of total volatile hydrocarbons and methane in the unsaturated zone immediately above the water table reflects that of dissolved organic carbon in the upper meters of the saturated zone, suggesting that gas samples from wells can be used to delineate contaminant plumes rapidly under some circumstances. Shallow samples were reliable indicators of contamination where petroleum floats on the water

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[1] U.S. Geological Survey, St. Paul, Minn.

table. However, hydrocarbon vapor concentrations decrease about 1,000-fold from land surface to a depth of about 4 m.

Nearly all of the volatile hydrocarbons measured except methane are almost completely oxidized before reaching land surface. This suggests that the natural system can almost entirely assimilate the contaminants. Moreover, the potential for large variations in vertical concentrations owing to microbial oxidation needs to be accounted for when interpreting the results of near-surface sampling for plume delineation. The major decrease in the partial pressure of oxygen and increase in that of carbon dioxide suggests that these gases may also be useful indicators of major contamination.

MATHEMATICAL MODELING OF HYDROCARBON AND OXYGEN TRANSPORT COUPLED WITH MICROBIAL DEGRADATION IN THE UNSATURATED ZONE

By Arthur L. Baehr[1] and Marc F. Hult[2]

A mathematical model of the simultaneous transport of hydrocarbons and free oxygen by advection and diffusion has been developed to test the hypothesis that microbial degradation rates in the unsaturated zone are controlled by the rate at which oxygen can diffuse into the contaminated region. Vapor distributions of free oxygen and hydrocarbons in the unsaturated zone at the Bemidji, Minn., research site indicate that this modeling approach may be a reasonable first approximation to the governing transport processes. The coupled model assumes that hydrocarbons are degraded at a rate determined by the stoichiometric equivalent of available free oxygen. This approach eliminates the need to model microbial populations explicitly.

[1] U.S. Geological Survey, Trenton, N.J.

[2] U.S. Geological Survey, St. Paul, Minn.

TRANSPORT AND FATE OF MONOAROMATIC HYDROCARBONS IN THE SUBSURFACE, BEMIDJI, MINNESOTA, RESEARCH SITE

By Robert P. Eganhouse[1], Thomas F. Dorsey[1], and Curtis S. Phinney[1]

Monoaromatic hydrocarbons comprise more than 90 percent of the nonpolar volatile organic substances present in ground water contaminated by crude oil at the research site near Bemidji, Minn. In order to better understand processes affecting the transport and fate of these compounds in the subsurface, water samples were taken at and below the water table in the vicinity of the oil body along a transect paralleling the direction of ground-water flow. Concentrations of 35 monoaromatic hydrocarbons, primarily benzene and C_1- through C_4-alkylated homologs, were determined in these samples by purge-and-trap gas extraction, chromatography/flame-ionization detection, and gas chromatography/mass spectrometry.

Benzene constitutes about 90 percent of the total monoaromatics in the ground water. All the possible C_2-, C_3-, and C_4-benzene isomers, except *t*-butyl benzene, have been identified in heavily contaminated samples. The concentration of benzene reaches a maximum of 3,400 micrograms per liter immediately downgradient from the oil body. This is substantially below the aqueous solubility of about 1,750 milligrams per liter. At the most distant well, 150 m (meters) farther downgradient, the concentration of benzene decreases by two orders of magnitude although it is still about an order of magnitude above the detection limit for the method. Thus, a minimum transport rate of approximately 7 centimeters per day can be estimated. Similar concentration decreases of two orders of magnitude are seen over vertical distances of less than 1 m below the water table. In general, the plume appears to reach greater depths with increasing distance from the oil body.

Because of their wide-ranging physicochemical properties and structural diversity, monoaromatic hydrocarbons serve as useful molecular probes of processes that affect the behavior of primary plume constituents. Changes in concentrations of dissolved aromatic hydrocarbons downgradient of the oil body reflect at least four processes: dispersion, volatilization, sorption, and microbial degradation. Differences in the apparent disappearance rates of isomeric assemblages of C_3- and C_4-benzenes and the *n*-alkylbenzene homology suggest that microbial degradation probably is the most important of these processes, at least in the immediate vicinity of the oil body. Evidence for rapid microbial metabolism of oil-derived organic matter in this near-field zone is found in the elevated concentrations of dissolved organic matter, methane, inorganic carbon, and reduced levels of dissolved oxygen. In this same anoxic zone, monoaromatic hydrocarbon concentrations decline most rapidly. The correlation of several alkylbenzene concentration maxima along the downgradient part of the transect may reflect periodic pulsing of source strength, perhaps in response to seasonal cycles such as recharge from snowmelt in spring. This hypothesis remains to be tested.

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[1] Environmental Sciences Program, University of Massachusetts, Boston, Mass.

NONVOLATILE ORGANIC ACIDS IN GROUND WATER CONTAMINATED WITH CRUDE OIL

By George R. Aiken[1], Kevin A. Thorn[1], and Myron H. Brooks[1]

A study of the composition and geochemical significance of nonvolatile organic acids resulting from the microbiological degradation of crude oil at the Bemidji, Minn., site was initiated in July 1986. Ground-water samples were collected from wells 530–B, 532–B, and 533–B, all of which are downgradient of the oil body and have dissolved organic carbon (DOC) concentrations of 14, 22, and 13 milligrams carbon per liter, respectively. DOC fractionation measurements on these samples indicate that the nonvolatile organic acids are a major constituent in the aquifer, accounting for approximately 60 percent of the DOC at each well.

The nonvolatile organic acids were isolated using XAD[2] resins. Each water sample was acidified to pH 2 and passed through a two column array consisting of XAD–8 followed by XAD–4. XAD–8, an acrylic ester resin routinely used to isolate aquatic humic substances, retained the more hydrophobic organic acids (such as long chain fatty acids) in the sample. XAD–4 is a styrene divinylbenzene resin with a greater surface area, and, in general, a greater capacity for lower molecular weight solutes than XAD–8. The fraction of the organic acids retained on the XAD–4 resin is more hydrophilic, with a greater concentration of carboxylic acid functional groups than the fraction retained on the XAD–8 resin. Initial studies on the chemical composition of the isolates involved gas chromatography-mass spectrometry (GC–MS) and ^{13}C nuclear magnetic resonance (NMR) spectroscopy. Preliminary GC–MS studies were accomplished by reacting the organic acids with boron trifluoride-methanol (BF_3-CH_3OH) to obtain the corresponding methyl esters. The sample was then separated on a DB–5 capillary column and chromatograms were obtained with a VG–7035 mass spectrometer. The resulting chromatograms indicate that these samples are a complex mixture of organic acids from the microbial degradation of the crude oil. Positive identification of individual compounds in these mixtures was hampered by the complexity of the chromatograms.

The solution state ^{13}C NMR analyses included the recording of quantitative spectra and attached proton test (APT) spectra. Quantitative spectra, which are acquired with inverse gated decoupling and long pulse delays, provided a quantitative measure of the distribution of the various carbon types present in the complex mixture of organic acids. The APT spectra differentiate among methyl, methylene, methine, protonated aromatic, nonprotonated aromatic, and quaternary carbons. The quantitative NMR spectra of the hydrophobic acids from all three wells exhibited virtually identical carbon distributions: 17 percent carboxyl carbon; 19 percent aromatic carbon; 7 percent secondary hydroxyl carbon; and 57 percent aliphatic carbon. The quantitative NMR spectra of the hydrophilic acids likewise showed that all three samples have nearly identical carbon distributions: 23 percent carboxyl carbon; 11 percent aromatic carbon; 18 percent secondary hydroxyl carbon; and 48 percent aliphatic carbon. The NMR spectra suggested that aromatic and isoparaffinic (branched chain + cyclic) components of the crude oil have been selectively preserved in the form of carboxylic acids, or, alternatively, that the partially degraded crude oil components have combined with the expired microbial biomass to form fulvic acidlike substances.

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

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

The nonvolatile organic acids at the Bemidji site are of potential geochemical significance. This fraction of the DOC pool is capable of interacting with organic compounds of low aqueous solubility, including components of the oil body, resulting in an enhancement of solubility and possible increased mobility of these low solubility components in the aquifer. These organic acids also act as complexing agents for trace metals resulting in the dissolution and transport of trace metals in the aquifer. Of particular geochemical interest at the Bemidji site is the potential role of these organic acids in the dissolution of silica.

CHARACTERIZING COLLOIDS IN NATURAL WATER

By Terry F. Rees[1] and James F. Ranville[1]

The role of colloidal materials has been largely neglected in studies of contaminant transport. A colloid is a finely dispersed phase having at least one dimension in the range of 1 to 1,000 nanometers. Due to the very small dimensions, colloids have specific surface areas which frequently exceed 500 square meters per gram. Because of this large surface area, colloids are efficient scavengers of heavy metals and organic pollutants. After sorption, movement of these pollutants will be controlled by the physical properties of the colloid rather than by the chemistry and physical properties of the unsorbed material.

The U.S. Geological Survey has undertaken a research program to study the behavior of colloidal materials in natural systems. The first phase of the program is to identify surface- and ground-water systems in which colloids are present. After identification of such systems, the colloids will be characterized as to size and shape distributions, chemical composition and crystal morphology, surface charge and surface-chemistry characteristics, and sorption of contaminants of interest. The transport of these colloid-contaminant associations will then be studied in field settings.

Techniques being used in this study include: (1) typical analytical techniques such as atomic absorption, inductively coupled plasma emission, and visible/ultraviolet spectroscopy; and (2) nontypical techniques such as scanning electron microscopy coupled with energy dispersive x-ray analysis (SEM/x-ray), photon correlation spectroscopy (PCS), electric birefringence analysis (EBA), and electrophoretic light scattering (ELS). The typical analytical techniques and SEM/x-ray are familiar to most researchers. PCS, EBA, and ELS are new techniques based on light scattering phenomena and have been reviewed in detail by Rees (in press). PCS provides information about translational diffusion coefficients (D_t) for dispersed colloids, and D_t is related to the particle-size distribution. EBA provides information about the rotational diffusion coefficient (D_r) which is related to the shape of dispersed colloids. ELS provides information analogous to typical electrophoretic measurements, but is applicable to much smaller particles.

Plans are to show how these various techniques can be used to determine the characteristics of colloidal populations in natural waters by using results obtained from field investigations at Bemidji, Minn., Pensacola, Fla., and the Whitewood Creek-Belle Fourche-Cheyenne River Basin investigation site.

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

MICROBIAL DEGRADATION OF PETROLEUM IN SUBSURFACE ENVIRONMENTS, BEMIDJI, MINNESOTA, RESEARCH SITE

By Fu-Hsian Chang[1], Nancy N. Noben[1], and Julie A. Bullert[1]

Laboratory research, in conjunction with field measurements, was conducted using upgradient (uncontaminated) and downgradient (contaminated) samples of sediment and ground water from a crude-oil-spill site near Bemidji, Minn.

Measurements of oxygen consumption, carbon dioxide (CO_2) production, and microbial biomass were used to interpret and compare rates of petroleum biodegradation. Microbial numbers in the ground water and sediment were enumerated by most probable number (MPN) using nutrient broth and Tauson's broth for total counts and petroleum degraders, respectively. Microbial biomass was assessed by the adenosine triphosphate (ATP) determination method as modified by Chang. Microbial degradation activity of petroleum was determined by the gravimetric method of residual oil and by the ^{14}C-hexadecane radioisotope method.

Field study indicates that linear correlation coefficients, $0.969 < \gamma^2 < 0.986$, were found between total microbial counts (number per gram sediment, or number per milliliter ground water) and ATP content (microgram ATP per gram sediment or nanogram ATP per milliliter ground water) in both sediment and ground-water samples (tables C–5 and C–6). Percentage of petroleum degraders in the sediment and ground water decreased with increasing distance downgradient from the oil-spill site. However, total microbial counts do not seem to correlate well with sample locations relative to the spill site. ATP contents also have good linear correlation ($\gamma^2=0.877$) with petroleum-degrader counts in sediment samples (table C–5). Petroleum-degrader numbers correlate well with microbial activity (high CO_2 partial pressure, high methane concentration, and low oxygen (O_2) partial pressure) as reported by Hult and Grabbe (1985). Total microbial counts, ATP contents, and degradation potential in the subsurface were greater below the water table than above the water-table environment in all sampling locations (table C–5). This implies that dissolution of hydrocarbon in water is an important factor for microbial degradation.

Table C–5.—*Number of petroleum degraders and adenosine triphosphate values in sediment samples collected at oil-spill site in July 1986*

[Values are means of three replicates. No./g = number per gram; µg/g = microgram per gram. Sample location: ug = upgradient and dg = downgradient. Depth: W.T. = water table; bwt = below water table; and awt, above water table]

Sample location (well number)	Depth (meters)	Total count (No./g sediment)	Petroleum degraders (No./g sediment)	Petroleum degrader (percent)	Adenosine triphosphate (µg/g sediment)
606 ug	at W.T.	3.0×10^5	2×10^3	0.67	0.198
603 ug	8.8–9.1 bwt	3.5×10^6	5×10^5	14.3	2.681
603 ug	7.3–7.6 awt	3.9×10^6	3.5×10^5	9.1	2.868
310E ug	at W.T.	1.7×10^6	7.2×10^6	.42	1.115

[1] Center for Environmental Studies, Bemidji State University, Bemidji, Minn.

Table C-5.—*Number of petroleum degraders and adenosine triphosphate values in sediment samples collected at oil-spill site in July 1986*—Continued

Sample location (well number)	Depth (meters)	Total count (No./g sediment)	Petroleum degraders (No./g sediment)	Petroleum degrader (percent)	Adenosine triphosphate (μg/g sediment)
[1]604A ug	7.8–7.9 bwt	$5.8x10^6$	$7.4x10^5$	13.0	4.366
607 dg	at W.T.	$1.1x10^7$	$1.9x10^6$	17.6	7.273
532D dg	8.4–8.5	$4.0x10^6$	$2.4x10^5$	24.0	2.554
532D dg	8.5–8.7	$3.2x10^6$	$1.0x10^6$	31.3	2.813
532D dg	8.8–9.0	$2.4x10^6$	$7.0x10^5$	29.2	2.136
533B dg	7.9–8.5 awt	$2.4x10^6$	$2.4x10^5$	10.0	1.789
533B dg	8.5–9.1 bwt	$2.4x10^6$	$9.0x10^5$	37.5	2.293
604A ug	5.0–5.2 awt	$6.0x10^6$	$7.4x10^5$	12.3	3.816
605 dg	9.1–9.4	$2.4x10^6$	$4.0x10^5$	16.7	1.926
605 dg	10.4–11.0	$2.4x10^6$	$2.2x10^5$	9.2	1.697

[1] Well 604A is located near the spill-site (35 meters upgradient).

Table C-6.—*Number of petroleum degraders and adenosine triphosphate values in ground-water samples collected at oil-spill site in August 1986*

[Values are means of three replicates. No./mL = number per milliliter; ng/mL = nanogram per milliliter. Sample location: ug = upgradient and dg = downgradient

Sample location (well number)	Total counts X 10^3 (No./mL ground water)	Petroleum degraders X 10^2 (No./mL ground water)	Petroleum degrader (percent)	Adenosine triphosphate (ng/mL ground water)
518 dg	4.77	8.13	17.1	2.876
531 dg	76.0	9.75	12.8	18.12
532A dg	6.35	9.28	14.6	3.653
532B dg	4.98	8.63	17.3	3.024
532C dg	3.32	7.51	22.6	2.206
532D dg	2.03	4.86	23.9	1.368
[1]421	6.91	47.3	68.5	8.011
533A dg	5.82	9.96	17.1	3.520
533B dg	3.75	8.77	23.4	2.523
533C dg	2.16	6.69	31.0	1.630
310E ug	85.4	1.94	.23	18.82
510 dg	3.38	5.42	16.0	2.005
513 dg	4.67	7.94	17.0	2.819
515A dg	3.68	.54	1.52	1.604
529 dg	2.92	.41	1.41	1.262
530A dg	3.11	4.76	15.3	1.860
530B dg	4.01	8.59	21.4	2.608
530C dg	1.55	3.45	22.3	1.026

[1] Spill site.

Sediment and ground-water samples were incubated with the addition of 1 percent petroleum or ^{14}C-hexadecane in microcosm condition. It was found that microbial degradation potential was significantly higher, $P \leq 0.01$, in samples that contained higher fractions of petroleum degraders than those with lower fractions of petroleum degraders. Oxygen consumption attained optimum conditions when added oil:N and oil:P ratios were 40 and 200, respectively, and samples were incubated for about 40 days at 7 °C. Oxygen consumption in ammonium nitrate (NH_4NO_3) amended samples decreased with C:N ratios of 40, 10, 20, and 60 in a decreasing order (fig. C–5). In phosphorus treated samples O_2-uptake decreased with C:P ratios of 200, 100, 150, and 400 (fig. C–6). Additions of high nitrogen (C:N ratios of 10 and 20) and high phosphorus (C:P ratios of 100 and 150) inhibited microbial respiratory activity and caused a slight fall of pH (0.4 to 0.8 units). Laboratory microcosm studies showed that a linear relationship ($\gamma^2=0.958$) was obtained between the radioisotope assay and gravimetric technique as a measure of ^{14}C-hexadecane and petroleum degradation by the indigenous microbial community at four temperature regimes (2, 7, 12, and 17 °C) after a 4-month incubation (fig. C–7). The quantity of CO_2 evolution and ^{14}C-recovery isotope assay are good measures for indigenous microbial potential to utilize petroleum and hexadecane. ATP content per unit of sediment or ground water was 17 to 35 percent higher during summer months than in winter months (table C–7). The length of incubation time required for a certain percentage of degradation of hydrocarbon was a measure of the density of hydrocarbon-degrading population in the subsurface environment (fig. C–8).

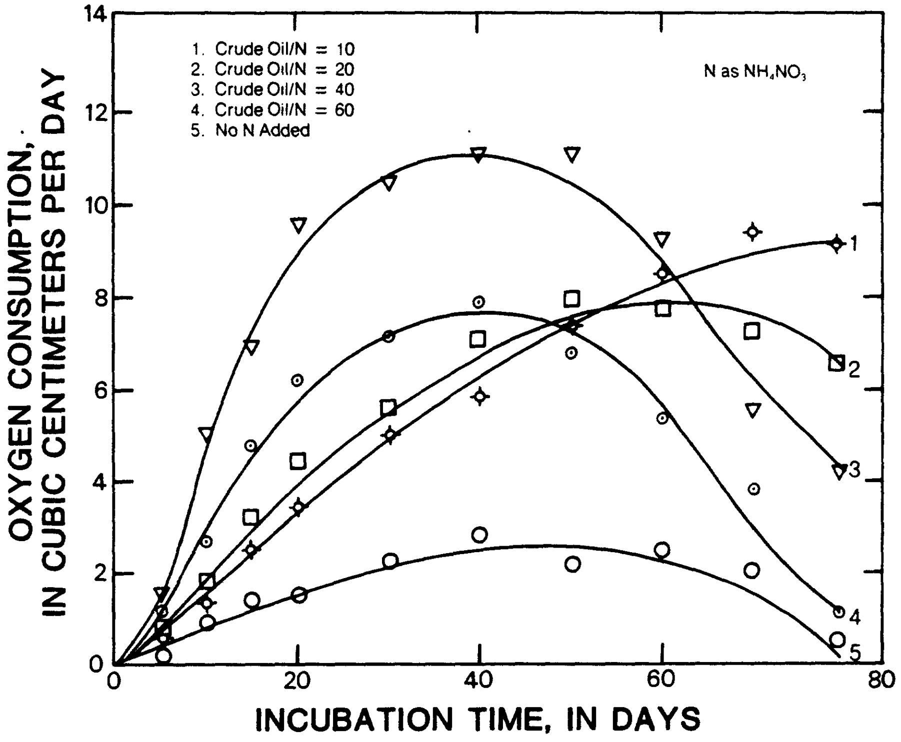

Figure C–5.—Effect of carbon:nitrogen ratios on oxygen consumption by indigenous micro-organisms in sediment and ground-water mixture.

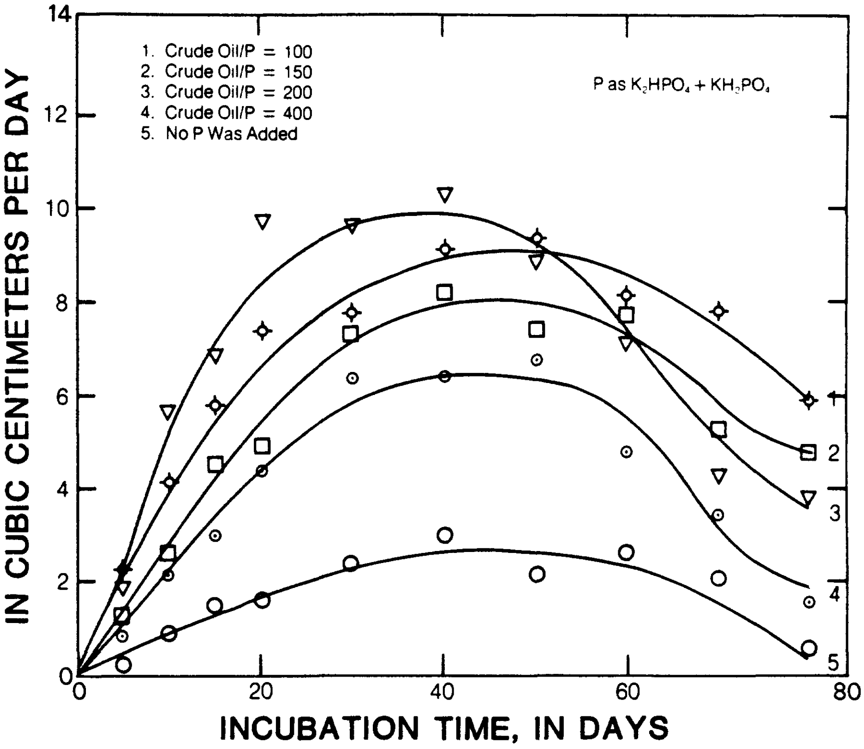

Figure C-6.—Effect of carbon:phosphorus ratios on oxygen consumption by indigenous micro-organisms in sediment and ground-water mixture.

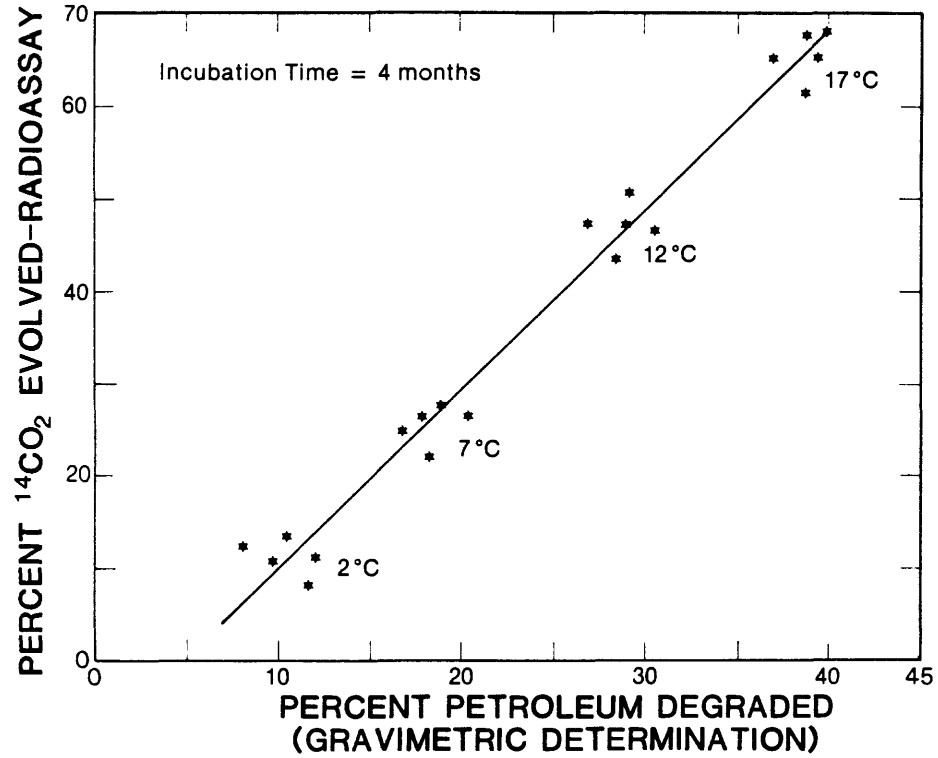

Figure C-7.—Comparison of microbial activity by radioisotope method and gravimetric determination method in sediment at four temperature regimes.

Table C-7.—*Seasonal variation of adenosine triphosphate values in ground water at oil-spill site*

[Values are means of three replicates. Ng/mL = nanogram per milliliter. Sample location: ug = upgradient and dg = downgradient

Sample location (well number)	Adenosine triphosphate (ng/mL ground water)		Seasonal variation (percent)
	Winter January 1987	Summer August 1986	
533A dg	2.518	3.520	28.0
533B dg	1.798	2.523	28.7
533C dg	1.334	1.630	18.2
513 dg	2.059	2.819	27.0
581 dg	1.897	2.876	34.0
[1]421	6.623	8.011	17.3

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[1] Spill site.

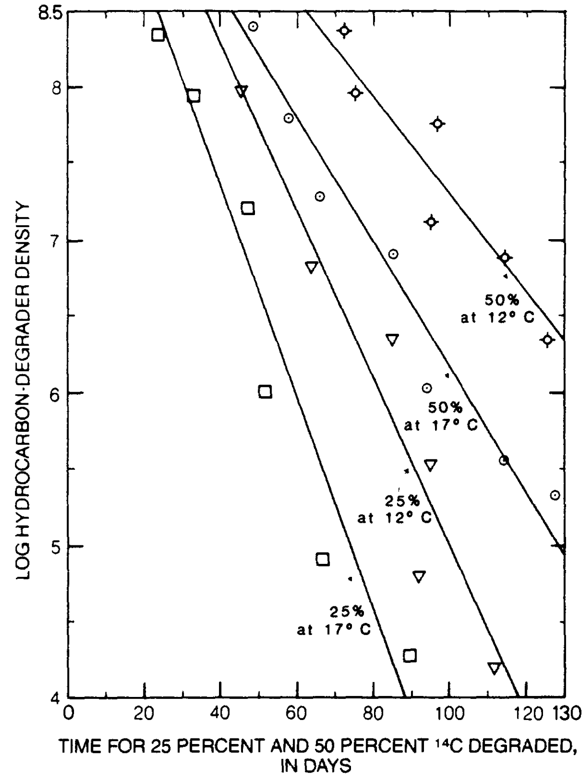

Figure C-8.—Duration of the 25 percent and 50 percent $^{14}CO_2$ evolution by indigenous cultures at different inoculum density.

REFERENCE

Hult and Grabbe, in press, Distribution of gases and hydrocarbon vapors in the unsaturated zone, *in* Ragone, S. E., U.S. Geological Survey's Toxic Waste—Ground-Water Contamination Program: Fiscal year 1986 program overview and selected abstracts from the October 21–25, 1985, technical review meeting, Cape Cod, Massachusetts: U.S. Geological Survey Open-File Report 86–481.

CHAPTER D.—ADDITIONAL TOXIC WASTE—GROUND-WATER CONTAMINATION PROGRAM RESEARCH

ILLUSTRATIONS

TABLES

CHAPTER D.—ADDITIONAL TOXIC WASTE—GROUND-WATER CONTAMINATION PROGRAM RESEARCH

INTRODUCTION

By Bernard J. Franks[1]

Most of the research associated with the U.S. Geological Survey Toxic Waste—Ground-Water Contamination Program has involved the three field demonstration areas described in chapters A, B, and C (this report). Because of the success of these interdisciplinary efforts, additional research efforts were begun at several sites nationwide. This chapter presents preliminary results from several of these investigations.

Chlorinated solvents, particularly trichloroethylene, are the subject of ongoing investigations by Fusillo and others. They discuss contamination, associated with the disposal of metal-plating wastes, of a glacial-stratified-drift aquifer.

Acidic ground-water contamination from copper mining in Arizona is discussed in two reports. Eychaner and Stollenwerk overview an alluvial aquifer, including public-supply wells, and an associated perennial stream contaminated by acid-mine drainage. In part II, Stollenwerk and Eychaner present results of laboratory column experiments which suggest that neutralization of hydrogen ions in the unconsolidated alluvium may be a principal mechanism for removing contaminants from the ground-water environment.

Methods of detection of selected pesticides, primarily weed-control agents, are the focus of Steinheimer's research. He analyzed for pesticide residues by both solid-phase extraction techniques and methanol extraction using a mechanical shaker.

Gasoline and diesel oil have contaminated the ground water at a site in Yakima, Wash. Ebbert describes the site and presents preliminary data on the behavior of petroleum contaminants in the subsurface.

Impact of pesticides and nitrogen compounds in a watershed in southwestern Georgia is discussed by Hicks and others. They present planned research involving the occurrence and movement of these compounds, and their effects on the hydrologic system.

All the papers referred to above appear in Chapter D of of this report: U.S. Geological Survey Open-File Report 87—109, entitled, "U.S. Geological Survey program on Toxic Waste—Ground-Water Contamination: Proceedings of the third technical meeting, Pensacola, Florida, March 23—27, 1987."

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[1] U.S. Geological Survey, Tallahassee, Fla.

MOVEMENT AND FATE OF CHLORINATED SOLVENTS IN GROUND WATER: PRELIMINARY RESULTS AND FUTURE RESEARCH PLANS

By Thomas V. Fusillo[1], Theodore A. Ehlke[1], Mary Martin[1],
and B. Pierre Sargent[1]

INTRODUCTION

The U.S. Geological Survey is conducting an interdisciplinary research study of ground-water contamination by chlorinated solvents and other contaminants associated with the disposal of metal-plating wastes at an arsenal in north-central New Jersey. The purposes of the study are: (1) to gain a better understanding of the chemical, physical, and biological processes that affect the movement and fate of chlorinated solvents, particularly trichloroethylene (TCE), in the subsurface, and (2) to develop predictive models of contaminant transport. The study area includes two waste-disposal sites that have contaminated part of the glacial-stratified-drift aquifer in the areas of Buildings 24 and 95 at the arsenal (fig. D–1). The site that is discussed here is the area affected by the disposal of metal-plating wastes at Building 24. This abstract summarizes the results of preliminary field investigations and outlines future research objectives.

The study area is located in the central part of the New Jersey Highlands—a region characterized by northeast to southwest-trending ridges separated by generally deep, narrow valleys. The arsenal is located in the Green Pond Brook Valley; the western boundary of the arsenal is at the edge of the terminal moraine of the Wisconsin glaciation. The valley north of the moraine contains unstratified and stratified drift. Hydrogeologic units underlying the study area consist of an unconfined stratified-drift aquifer, approximately 11 m (meters) in thickness; a confining unit of variable thickness; and a confined stratified-drift aquifer, ranging from 6 to 25 m in thickness, overlying bedrock. The depth to water ranges from about 1.5 to 5 m below land surface.

From 1960 to 1981, a metal-plating wastewater-treatment system in Building 24 discharged wastewater into an unlined filtration pit. Average wastewater discharge during 1979 was approximately 38,000 L (liters) per day, with a maximum daily discharge of 81,400 L. The infiltration of wastewater into the ground-water system has produced a plume of contaminants in the unconfined aquifer, which emanates from the area of Building 24 and follows the general water-table gradient. The most significant contamination is limited to the unconfined aquifer; however, because of seepage around or through the confining unit, TCE has been detected in some wells in the confined aquifer.

TCE is the predominant contaminant in the plume; other organic compounds detected include tetrachloroethylene, 1,1,1-trichloroethane, 1,2-cis dichloroethylene, and vinyl chloride. Elevated levels of several inorganic constituents have been detected, including cadmium, chromium, lead, selenium, cyanide, and copper. Recent data, however, show that concentrations of most inorganic constituents in the ground water have decreased significantly since 1981.

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[1] U.S. Geological Survey, West Trenton, N.J.

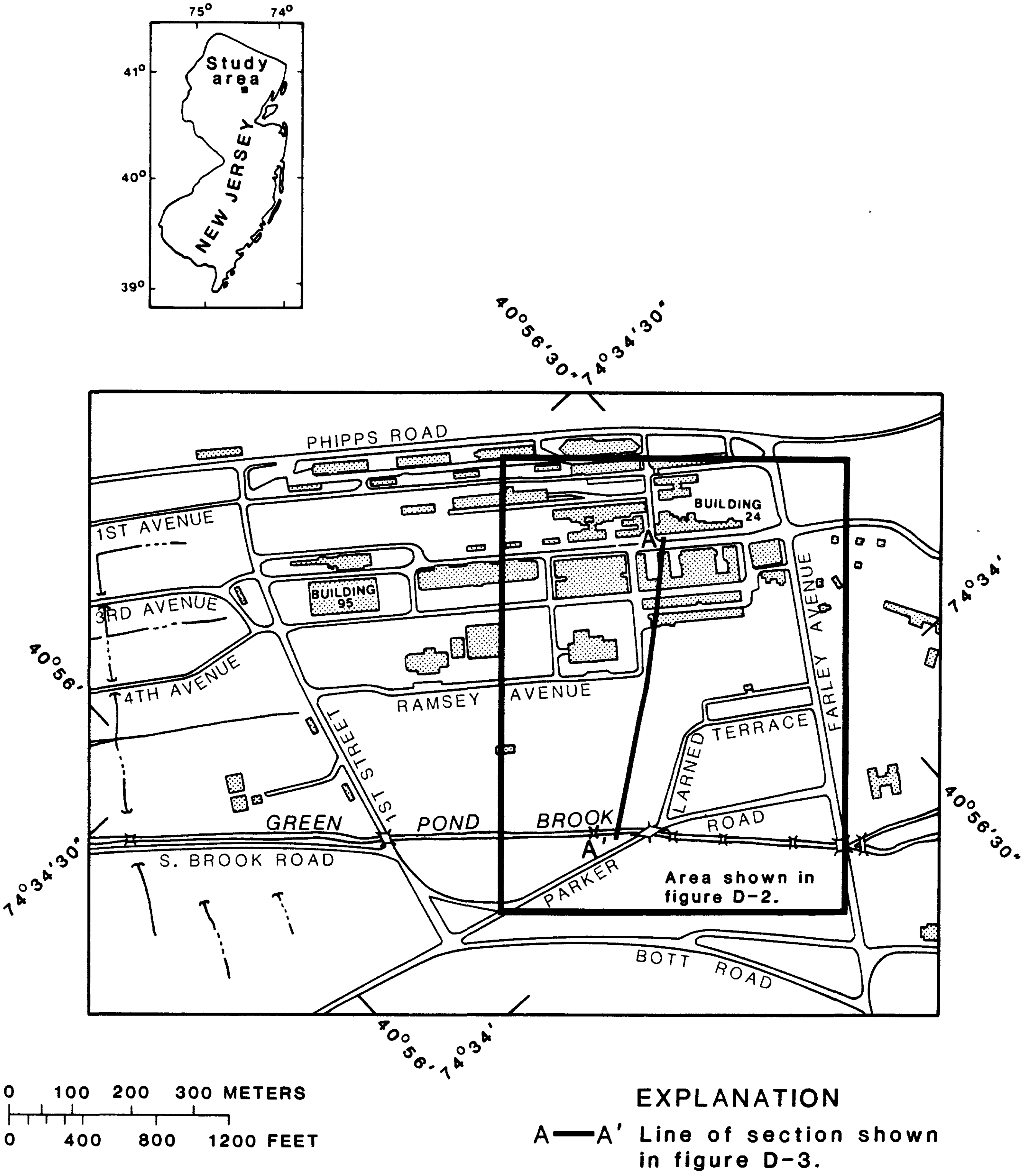


Figure D-1.—Location of study area in north-central New Jersey.

PRELIMINARY RESULTS

During 1986, extensive sampling and analysis of ground water was conducted. In order to define the three-dimensional distribution of chemical constituents in the unconfined aquifer, a drive-point ground-water sampling device was used to collect vertically spaced samples at 15 sites in the area around Building 24. A total of 120 samples was collected for analysis of volatile organic compounds, and 60 samples for analysis of common ions, nutrients, trace metals, and dissolved methane. Based on the results of these analyses, areal distributions of TCE, 1,2-cis-dichloroethylene, dissolved organic carbon, and dissolved methane are shown in figure D–2. Although TCE was the most frequently detected volatile organic compound, 1,2-cis-dichloroethylene (a breakdown product of TCE) was detected at most sites. Vinyl chloride and dissolved methane also were detected at several sites. Those areas containing the highest methane concentrations also contained the highest concentrations of vinyl chloride and no detectable nitrate, indicating strongly reducing conditions. Significant vertical variability in the concentrations of organic and inorganic constituents was observed at most of the 15 sites sampled. A generalized geohydrologic section showing TCE concentrations along the approximate center of the plume is shown in figure D–3.

RESEARCH HYPOTHESES AND APPROACHES

Planned research topics in this study have been divided into four broad areas of research. Some preliminary research hypotheses that may be tested and possible approaches for each area of research are discussed below.

Distribution and Movement of Chlorinated Solvents in Ground Water

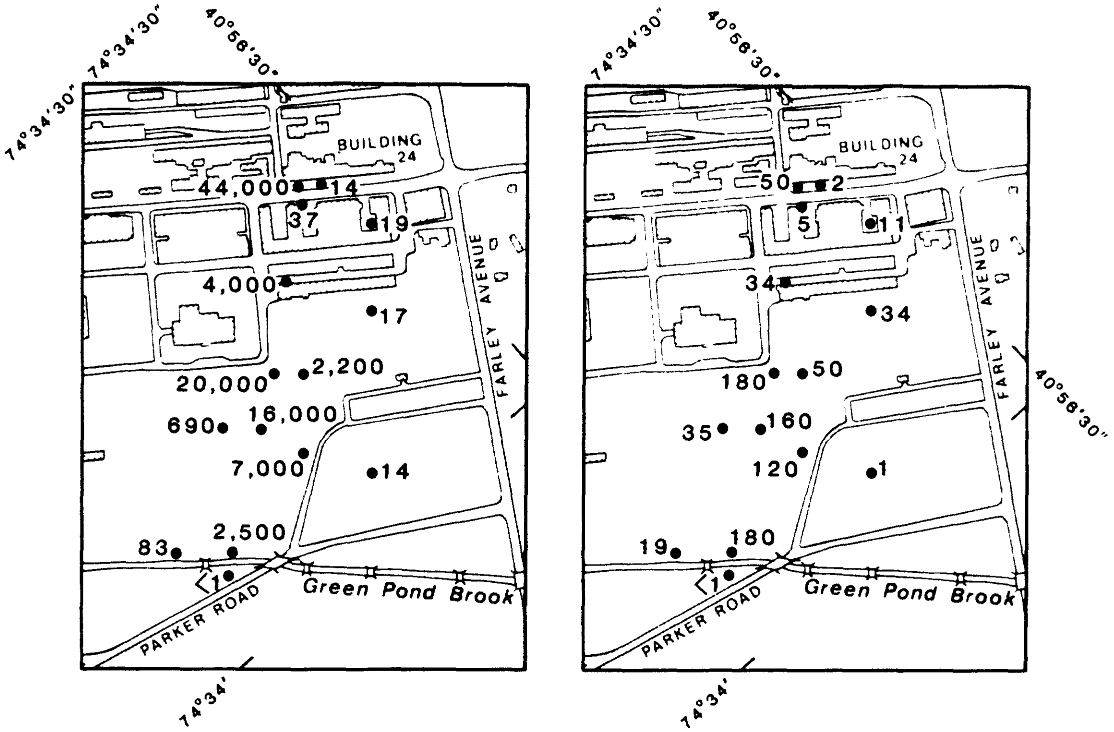
Hypotheses

- The observed distribution of trichloroethylene in ground water is largely the result of transport of solutes by ground-water flow.
- The movement of contaminants is significantly affected by geologic and hydrologic conditions in the study area.
- The movement of selected inorganic and organic constituents in the ground water can be simulated with a solute-transport model.

Possible approaches

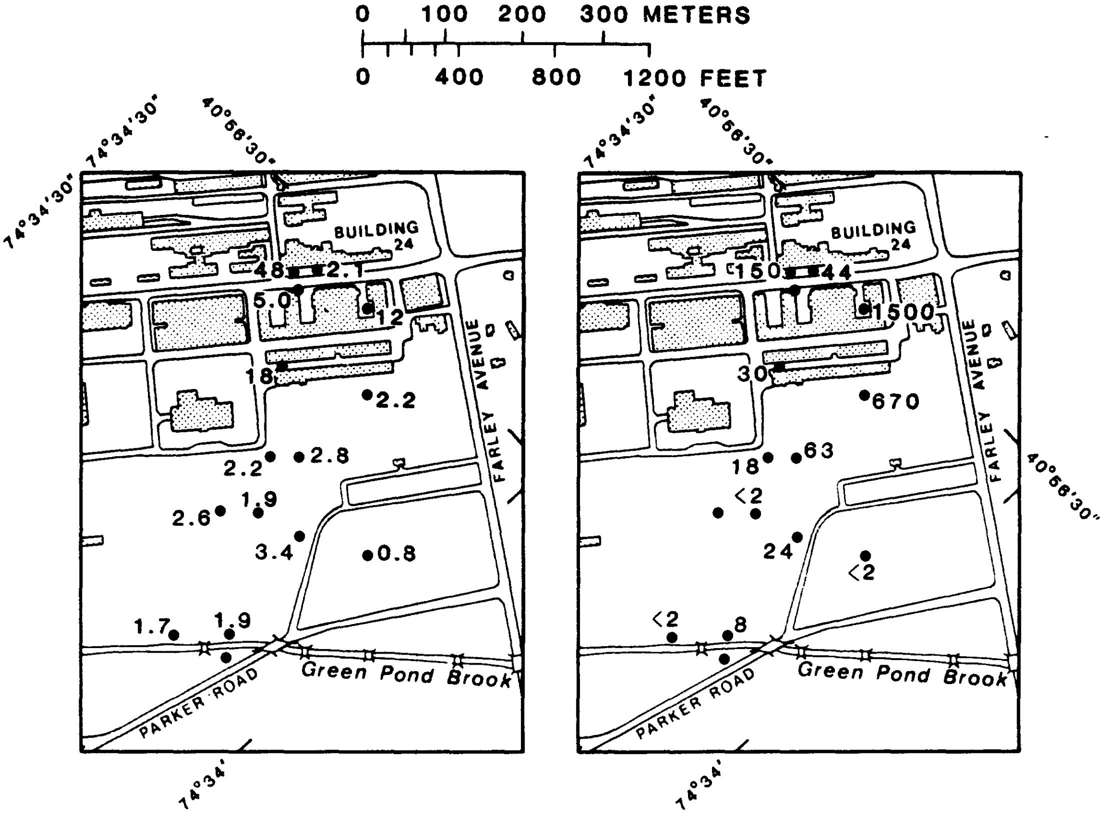
- Install several nests of monitoring wells in the study area.
- Collect samples of aquifer and confining units during drilling operations.
- Perform physical and chemical analyses of the geologic samples.
- Analyze ground-water samples for inorganic and organic constituents.

A preliminary three-dimensional flow model has been developed, based on previously collected hydrogeologic data, for the southwestern part of the Arsenal. This model simulates flow in three aquifers: the unconfined glacial aquifer, the confined glacial aquifer, and the bedrock aquifer. A more detailed three-dimensional flow model is being developed to improve the definition of flow conditions in the study area.



a.) Trichloroethylene, in micrograms per liter

b.) 1,2-cis-dichloroethylene, in micrograms per liter



c.) Dissolved organic carbon, in milligrams per liter

d.) Dissolved methane, in micrograms per liter

Figure D-2.—Areal distribution of: (a) trichloroethylene, (b) 1,2-cis-dichloroethylene, (c) dissolved organic carbon, and (d) dissolved methane. Values represent maximum concentrations detected at each site.

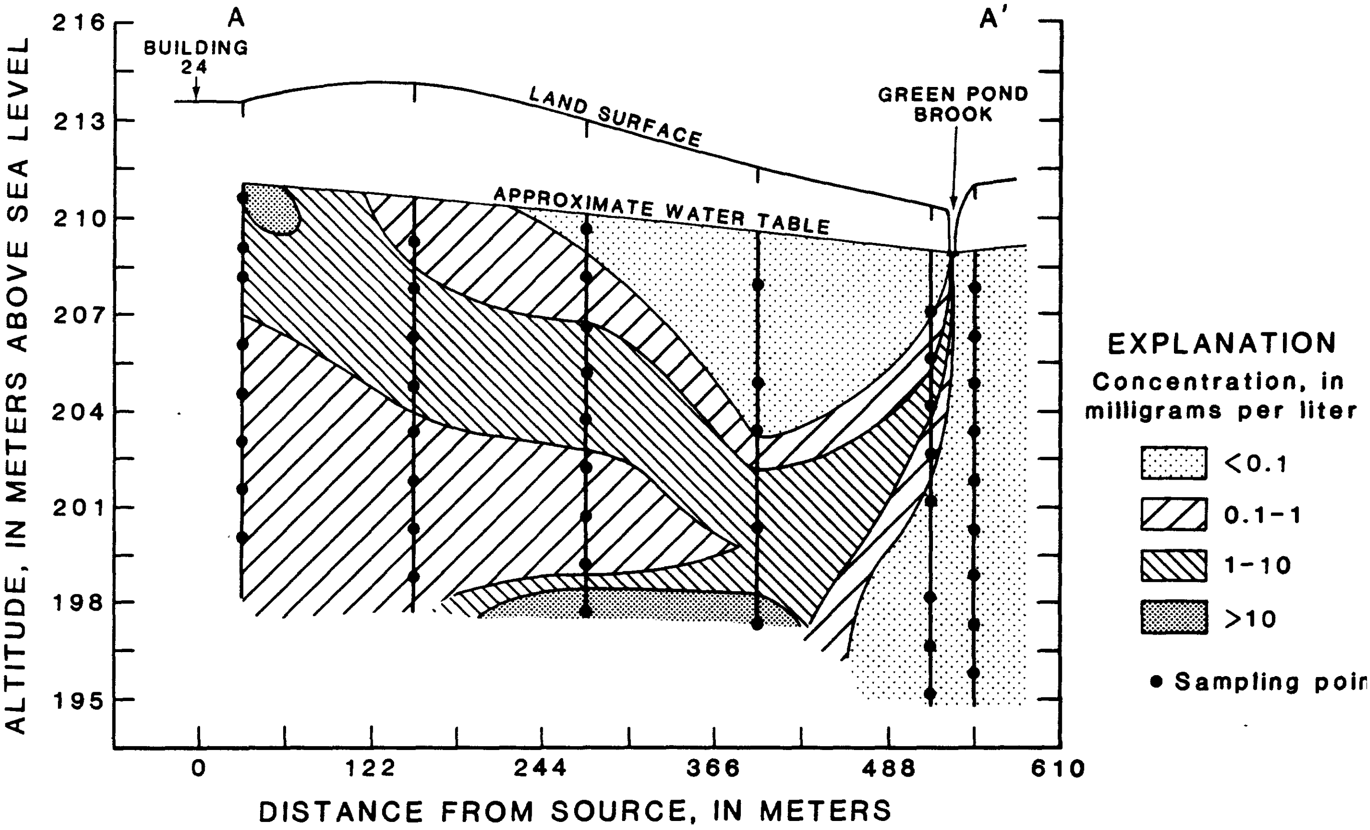


Figure D-3.—Generalized vertical distribution of trichloroethylene along section A-A' through approximate center of the plume. Location of section shown on figure D-1.

- Use the flow system, defined by this model, to develop the framework for several smaller scale flow and solute transport models, which can be used to define the movement of single constituents. The flow and solute transport models should have the same geohydrologic framework as the larger scale flow model but have a finer discretization scale and incorporate lateral boundary flows calculated from the three-dimensional flow simulations.

Geochemistry of Contaminated Ground Water

Hypotheses:

- Ground-water chemistry is affected by the composition and concentration of contaminants and chemical processes occurring in the ground water. These processes include sorption/desorption, volatilization, ion exchange, dissolution/precipitation, and oxidation-reduction reactions.

- The size and composition of aquifer particles, as well as the surface coatings on the particles, affect the interactions between solutes in the ground water and the aquifer material.

Possible approaches

- Perform analyses of water and geologic samples using purge-and-trap gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS), liquid extraction GC/MS, and atomic-absorption spectrophotometry to provide data on contaminant composition and concentrations in the aqueous and solid phases of the ground-water system.

- Analyze selected samples for dissolved gases.

- Obtain sorption data for selected contaminants from laboratory batch or column experiments using aquifer sediments.

- Analyze samples of aquifer and confining unit material by x-ray diffraction to determine mineralogic composition and by x-ray fluorescence to determine elemental composition.

- Examine samples of ground water and aquifer sediments from various points in the contaminant plume to determine the chemical and physical processes controlling contaminant movement and to identify reaction sequences occurring through the length of the contaminant plume.

- The approach and methods to be used in studying the sediment coatings have not yet been defined; however, the effects of the coatings on the movement of contaminants is probably significant and should be an important area of study.

- Equilibrium models may be used to test hypotheses about reactions occurring in the contaminant plume, where appropriate.

Microbial Transformations of Chlorinated Solvents

Hypotheses

- Microbial activity is a major factor influencing the transport and fate of organic contaminants, including TCE, in both the saturated and unsaturated zones.

- *In-situ* biodegradation is controlled by a complex series of physical, chemical, and biological interactions. The rate and biotransformation pathways differ in the saturated and unsaturated zones.

- Microbial activity varies greatly in different areas of the ground-water contamination plume.

Possible approaches

- Collect and analyze water samples from selected sampling points within and outside the area of contaminated ground water for compounds that may be indicators of microbial activity. These compounds include vinyl chloride, 1,2-trans-dichloroethylene, and 1,2-cis-dichloroethylene.

- Analyze samples for major ions; nutrients; and dissolved gases, including oxygen, carbon dioxide, nitrogen, hydrogen, and methane.

- Measure pH, specific conductance, temperature, and Eh.

- Measure microbial biomass using methods such as the Acridine Orange direct count and the agar spread-plate count.

- Collect samples of ground water and aquifer material to study the role of microorganisms in biotransformation and biodegradation of chlorinated solvents.

- Use laboratory studies of soil and aqueous microcosms to simulate biodegradation in the saturated and unsaturated zones. Of particular interest are the relations among the biotransformation of chlorinated solvents and other biotransformation processes, such as methanogenesis, sulfate reduction, and denitrification.

- Amend laboratory microcosms with various substrates to study enhanced biodegradation.

- Soil-column studies, with growth-stimulating amendments and varying soil-gas conditions, could later be performed as a model-cleanup process.

Chlorinated Solvents in the Unsaturated Zone

Hypotheses

- Retention of organic solutes in the unsaturated zone is controlled by the organic-carbon content and moisture content of the soil, as well as by the particle size and mineral composition of the soil.

- Movement of volatile contaminants from the ground water through the unsaturated zone to the atmosphere is limited because of the large paved area around Building 24 and the vertical distribution of contaminants in the ground water.

- Desorption of organic contaminants from the unsaturated zone is a continuing source of contaminants to the ground-water system.

- Air venting of the unsaturated zone can be applied to consolidate monitoring of soil gases and to remove sorbed contaminants from the unsaturated zone.

Possible approaches

- Collect soil samples from various points in the unsaturated zone.

- Extract samples at selected depths for analysis of organic compounds.

- Perform analyses to determine the particle-size distribution, organic-carbon content, water content, and clay mineralogy of the soils.

- Collect ground-water samples from the top of the water table at each site to determine contaminant levels.

- Determine (from laboratory experiments done on samples of contaminated aquifer material) the potential for leaching of organic contaminants from the sediments.

- Determine (from laboratory experiments with samples of uncontaminated aquifer material) the sorption properties of the soil and the role of organic carbon and moisture content in controlling sorption.
- Define the three-dimensional distribution of contaminants and gases in the unsaturated zone by collection of soil-gas samples from vapor probes installed at selected locations. A mobile GC/MS may be available to perform on-site chemical analyses of soil-gas samples.
- The use of air venting of the unsaturated zone, both as a method of consolidating unsaturated zone monitoring and as a remedial measure to remove sorbed contaminants may be investigated. The preliminary analyses associated with this effort would include *in-situ* measurements of permeability and air-filled porosity in the unsaturated zone.

ACIDIC GROUND-WATER CONTAMINATION FROM COPPER MINING NEAR GLOBE, ARIZONA: I. OVERVIEW

By James H. Eychaner[1] and Kenneth G. Stollenwerk[2]

Water that contains elevated concentrations of dissolved metals and sulfate at pH as low as 3.6 is moving through an alluvial aquifer and affecting surface streams near Globe, Ariz. (fig. D-4). Several public-supply wells have been contaminated, and a perennial stream rising from the aquifer has the potential to degrade public water supplies for Phoenix, Ariz., 130 km (kilometers) west of the study area. Dissolved-solids concentration of the outflow has increased about 50 mg/L (milligrams per liter) annually since 1980. A major source of the contamination is leakage through mine waste and tailings piles from unlined ponds with pH as low as 0.7 (Envirologic Systems, Inc., 1983, p. 10). Copper minerals have been mined from granite porphyry adjacent to the aquifer since 1903 (Peterson, 1962).

The objectives of this study are to define the extent of the contamination, evaluate rates of movement, and test laboratory models of reaction chemistry in a field setting. The study began in May 1984 and focuses on the movement and fate of the contaminants in the undisturbed part of the aquifer. Previous reconnaissance studies of water-quality problems in the vicinity emphasized the lands disturbed by mining.

Peterson (1962) described the geology of the southern part of the study area. The Gila Conglomerate (Tertiary to Quaternary age), which forms the bulk of the aquifer, is bounded by low-permeability rocks on the west, north, and east (fig. D-5). The Gila Conglomerate was formed by several broad alluvial fans that deposited unsorted angular rubble, well-rounded pebbles and cobbles, and firmly cemented sand and silt. East-trending faults broke these sediments into three blocks, the northernmost of which includes fine-grained lakebed deposits (D. R. Pool, U.S. Geological Survey, written commun., 1984). The Gila Conglomerate is more than 1,200 m (meters) thick about 2 km south of the head of Miami Wash (Peterson, 1962, p. 41), but it is less than 100 m thick about 6 km farther north (Pinto Valley Copper Corporation, written commun., 1967). The hydraulic conductivity of the conglomerate is on the order of 0.03 m/d (meter per day).

Unconsolidated alluvium has been deposited along Miami Wash and Pinal Creek north of Miami Wash in a band 300 to 800 m wide and as much as 50 m thick. Alluvium generally overlies the Gila Conglomerate and consists of reworked conglomerate and material eroded from older rocks in sizes from clay to boulders. Fine sand to coarse gravel predominate; finer and coarser materials generally are found in local lenses or stringers. Alluvium is also present along Pinal Creek upstream of Miami Wash but is generally less than 50 m wide. Hydraulic conductivity of the alluvium is on the order of 200 m/d.

Streamflow is generally ephemeral except in the northern 5 km of the area, where the cross-sectional area of the aquifer is reduced. At the northern boundary of the study, low-permeability rocks force the entire ground-water flow to the surface to produce perennial flow. Discharge from the aquifer was 0.2 to 0.4 cubic meter per second during 1980-86.

[1] U.S. Geological Survey, Tucson, Ariz.

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

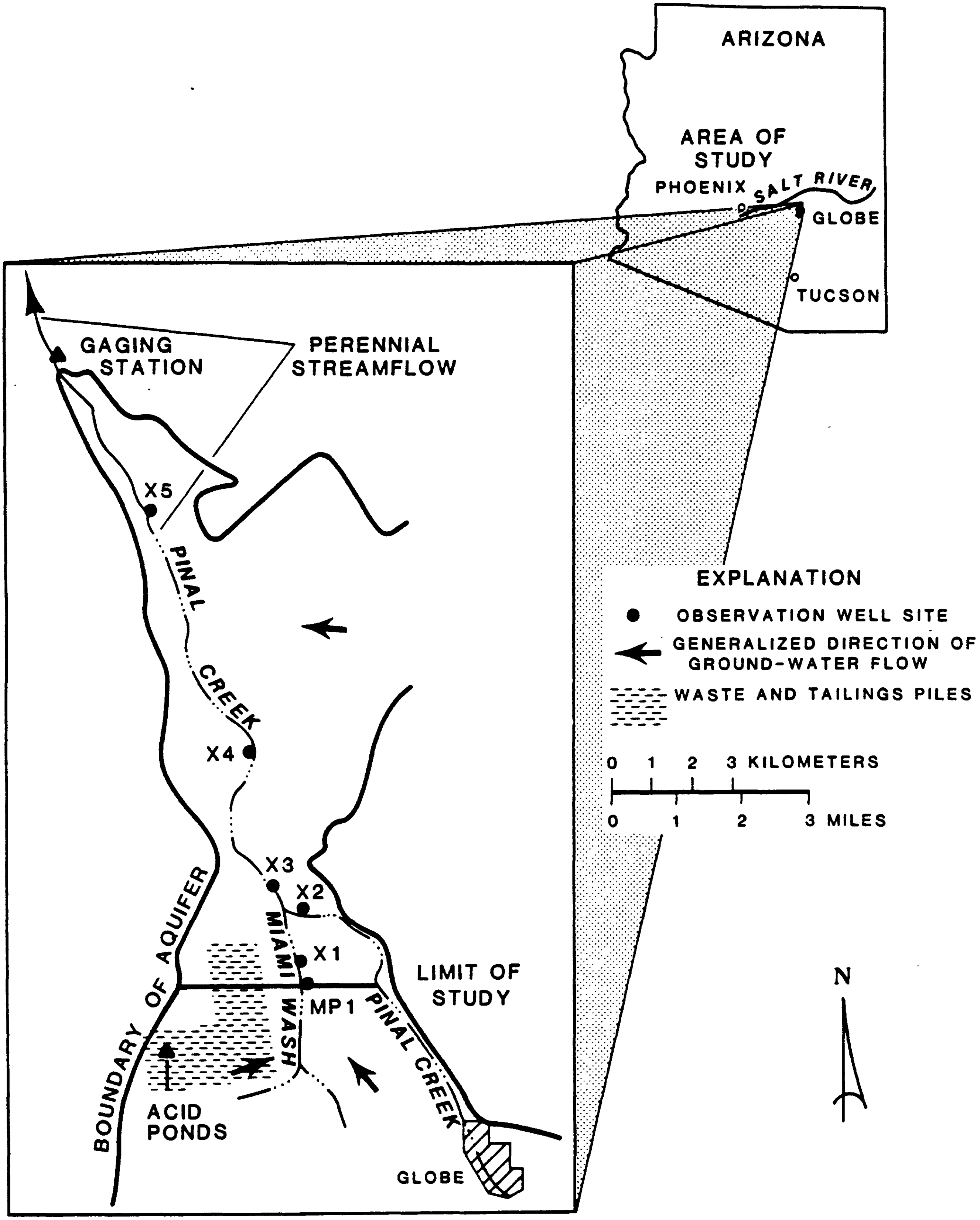


Figure D-4.—Area of study near Globe, Arizona.

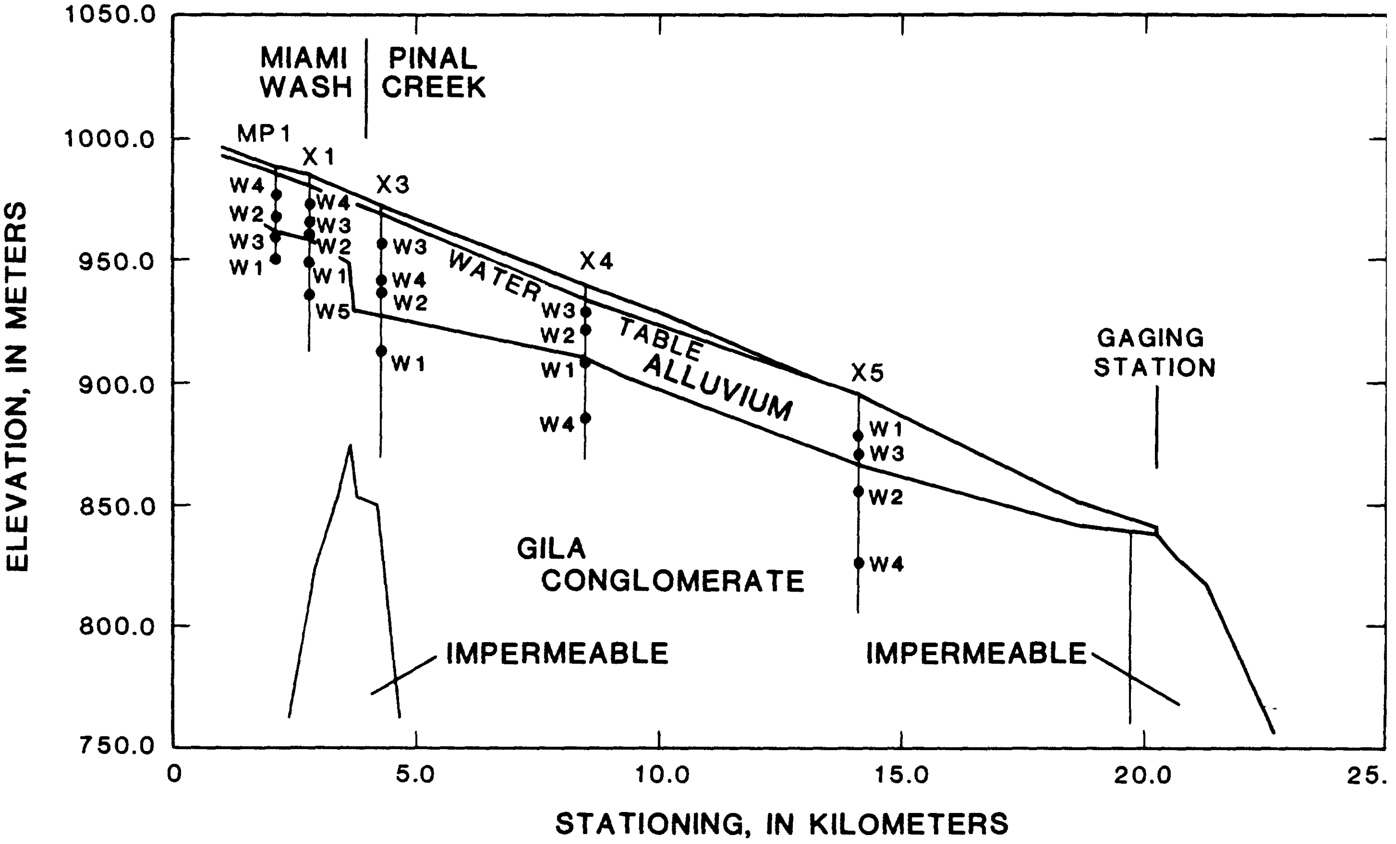


Figure D–5.—Simplified longitudinal section of the aquifer.

Previous studies suggested a simple conceptual model of contaminated alluvium and uncontaminated conglomerate, but field data promptly forced the model to change. At 6 sites (fig. D–4), 23 wells were completed using solvent-welded 102-millimeter polyvinyl chloride (PVC) casing with 0.9 m of slotted screen. Construction and sampling details were given by Eychaner and Stollenwerk (1985). Further exploratory drilling using a dual-wall air-rotary rig provided greater detail about the vertical variation of lithology and solution chemistry. The depths of most observation wells are shown on the longitudinal geologic section of the valley (fig. D–5).

Water in the area is either uncontaminated, acidic, or neutralized (table D–1); Eychaner and Stollenwerk (1985) described the geochemisty of the transitions between types. Water affected by contamination was found at least 30 m into the conglomerate at all sites. In most of the area solution chemistry shows a continuous vertical variation, but the most downstream site (X5) has three distinct layers of uniform chemistry (fig. D–6).

Both geologic units act as a single aquifer in dynamic equilibrium with varying recharge. Water levels show both seasonal and long-term variation. Head relations among wells at each site showed rapid movement of water from the alluvium to the conglomerate during recharge episodes and flow reversal at other times. Contaminated water is moving along nonequilibrium flow paths and being modified by reactions with minerals in the aquifer.

Table D-1.—*Representative analyses of ground water*

[Values in mg/L except as noted. < = below analytical detection limit]

Property	Well number		
	X5W4	MP1W1	X5W1
Sample date	11-6-86	3-21-85	11-6-86
Water type	Uncontaminated	Acidic	Neutralized
Geologic unit	Gila Conglomerate	Gila Conglomerate	Alluvium
Depth, meter	70	35	17
pH	7.7	3.6	6.1
Conductance, $\mu S/cm$	430	11,000	3,500
Calcium (Ca)	47	480	650
Magnesium (Mg)	16	390	150
Sodium (Na)	26	230	76
Bicarbonate (HCO_3)	210	0	140
Sulfate (SO_4)	27	9,800	2,100
Chloride (Cl)	10	310	98
Silica (SiO_2)	29	110	63
Oxygen (O_2)	6.0	.1	.4
Aluminum (Al)	<	310	<
Cadmium (Cd)	<	.4	<
Cobalt (Co)	<	13	<
Copper (Cu)	<	170	<
Iron (Fe)	<	3,100	<
Manganese (Mn)	.1	77	47
Nickel (Ni)	<	4.1	.3
Strontium (Sr)	.3	1.3	2.2
Zinc (Zn)	<	22	<

The question of when acidic water might begin to arrive in the perennial reach of Pinal Creek can now be addressed semiquantitatively. Acidic water pumped through a laboratory column of alluvium reacted to maintain outflow pH above 7 until all carbonate was dissolved, after which pH fell rapidly to about 4 (Stollenwerk and Eychaner, Chapter D, this report). At site X5, 0.5 km downstream from the head of perennial flow, water in the alluvium had a pH of 6.1 in late 1986, which suggests a possible rapid pH decrease in the near future.

Ground water under much of Miami Wash was acidic by 1945. Steel well casings about 0.5 km north of site X1 were replaced in 1945 after about 25 years service, but they had to be replaced again in 1947 (Chris Erskin, Pinto Valley Copper Corporation, oral commun., 1987). By 1982, pH 4 water was at least 1 km north of site X4; the acid front had advanced at least 6 km in 37 years, or about 1 km every 6 years. The present location of the acid front is unknown, but it is probably 2 to 3 km south of the beginning of perennial flow. Because of the large uncertainties in estimating the front's location and velocity, an initial breakthrough of acidic water to the perennial stream in 5 years would not be surprising.

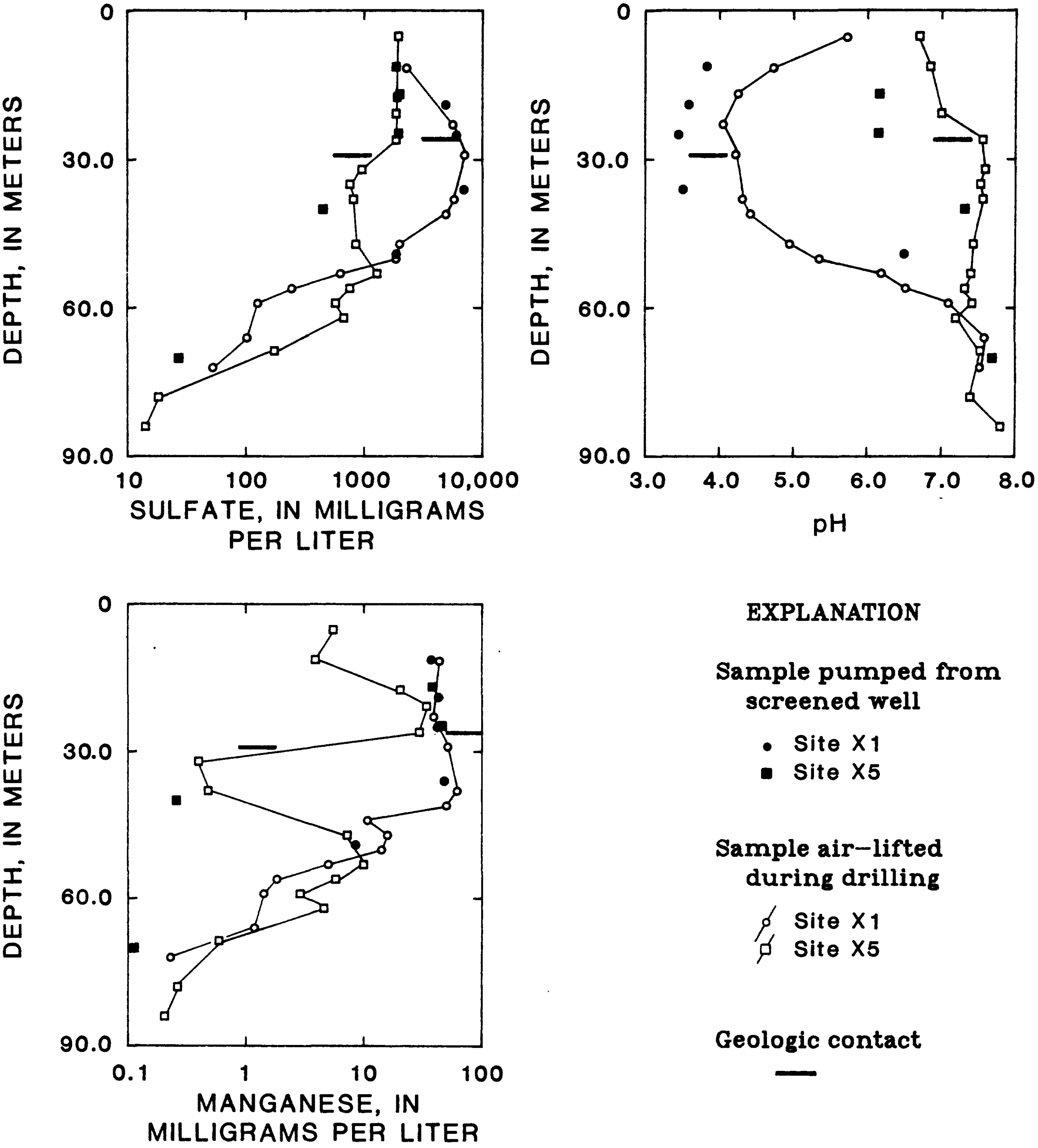


Figure D–6.—Variation of water quality with depth.

In July 1986, the U.S. Environmental Protection Agency issued a finding and order directing one mine to drain or line the acidic ponds near its plant and to begin some aquifer restoration. On the basis of the breakthrough estimates above, the order was modified to require exploration on company property to more closely identify the location of the acid front.

With an adequate base of descriptive data on hand, numerical modeling of flow in the aquifer has begun. Plans are for the flow model to be succeeded by a model of conservative solute transport, probably for chloride. Finally, plans are for models of reactive transport to be developed from laboratory data and tested against the field data.

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Stollenwerk, K. G., and Eychaner, J. H, 1987, Acidic ground-water contamination from copper mining near Globe, Arizona: II. Neutralization capacity of alluvium, *in* Franks, B. J., ed., U.S. Geological Survey program on Toxic Waste—Ground-Water Contamination: Proceedings of the third technical meeting, Pensacola, Florida: U.S. Geological Survey Open-File Report 87–109, p. D-19–D-24.

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ACIDIC GROUND-WATER CONTAMINATION FROM COPPER MINING NEAR GLOBE, ARIZONA: II. NEUTRALIZATION CAPACITY OF ALLUVIUM

By K. G. Stollenwerk[1] and J. H. Eychaner[2]

INTRODUCTION

The U.S. Geological Survey is conducting a study of acidic ground-water contamination from copper mining near Globe, Ariz. One of the goals of this study is to predict when the acidic ground-water plume will reach the zone of ground-water discharge to Pinal Creek. To accomplish this goal, an estimate of the capacity of the alluvium for removing constituents from the acidic ground water is required. Laboratory column experiments are one means of obtaining this data; results to date are presented here.

METHODS

Two types of alluvium were used in the column experiments. One sample was collected from a small, abandoned gravel quarry located upstream from where the acidic plume enters the alluvium along Pinal Creek. This alluvium is mineralogically similar to drill cuttings collected from the contaminated alluvium downgradient. Batch experiments have confirmed that most of the unconsolidated alluvium along Pinal Creek reacts with the acidic ground water to a similar extent. The second sample is carbonate cemented Gila Conglomerate collected from an outcrop along the edge of Pinal Creek, and is the same material that underlies the unconsolidated alluvium. The major difference between both samples is a greater carbonate content in the Gila Conglomerate.

Acidic ground water was collected from well MP1W1 in Pyrex[3] bottles and maintained at 4 °C until needed. Uncontaminated ground water was collected from well X2W2, upstream from the plume. Concentrations of the elements discussed in this paper are given in table D–2. Details of the water chemistry have been previously presented (Eychaner and Stollenwerk, 1985).

Table D–2.—*Concentrations of aluminum, copper, and iron, and pH of acidic ground water and uncontaminated water*

[Concentrations are in milligrams per liter; < = below analytical detection limit]

Ground water	pH	Aluminum	Copper	Iron[1]
Acidic	3.5	314	168	3,110
Uncontaminated	7.2	<	<	<

[1] Iron is in the ferrous oxidation state.

Columns 80 cm (centimeters) in length by 5 cm inside diameter were packed with <2-mm (millimeters) size alluvium and placed in a glove box under a nitrogen atmosphere. Uncontaminated ground water was eluted through

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

[2] U.S. Geological Survey, Tucson, Ariz.

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

the columns until effluent concentrations reached steady state at which time the influent was switched to acidic ground water, denoted by pore volume zero in subsequent figures. Flow rates averaged 25 cm/d (centimeters per day); thus, approximately 3 days were required to collect one pore volume of effluent. After constituents in the column containing unconsolidated alluvium had attained breakthrough, flow was stopped in both columns for an 11-month period to allow the acidic ground water and alluvium to reequilibrate. Flow of acidic ground water was then restarted. At pore volumes 11 (alluvium) and 14 (conglomerate), the influent was switched back to uncontaminated ground water, to evaluate the amount of ground water necessary to return effluent concentrations to background levels.

RESULTS AND DISCUSSION

Unconsolidated alluvium does not have a very large capacity for neutralizing H^+ (fig. D-7); this is consistent with the low carbonate content of the alluvium. The first pore volume of acidic ground water was completely and rapidly neutralized by carbonate minerals. The pH then dropped rapidly to about 4, followed by a much slower rate of decrease to approximately 3. Batch data, not presented here, also indicate two rates of H^+ neutralization. At this time it appears that the slower neutralization rate between pore volumes 3 and 11 is a result of reaction with the various igneous and metamorphic minerals present in the alluvium.

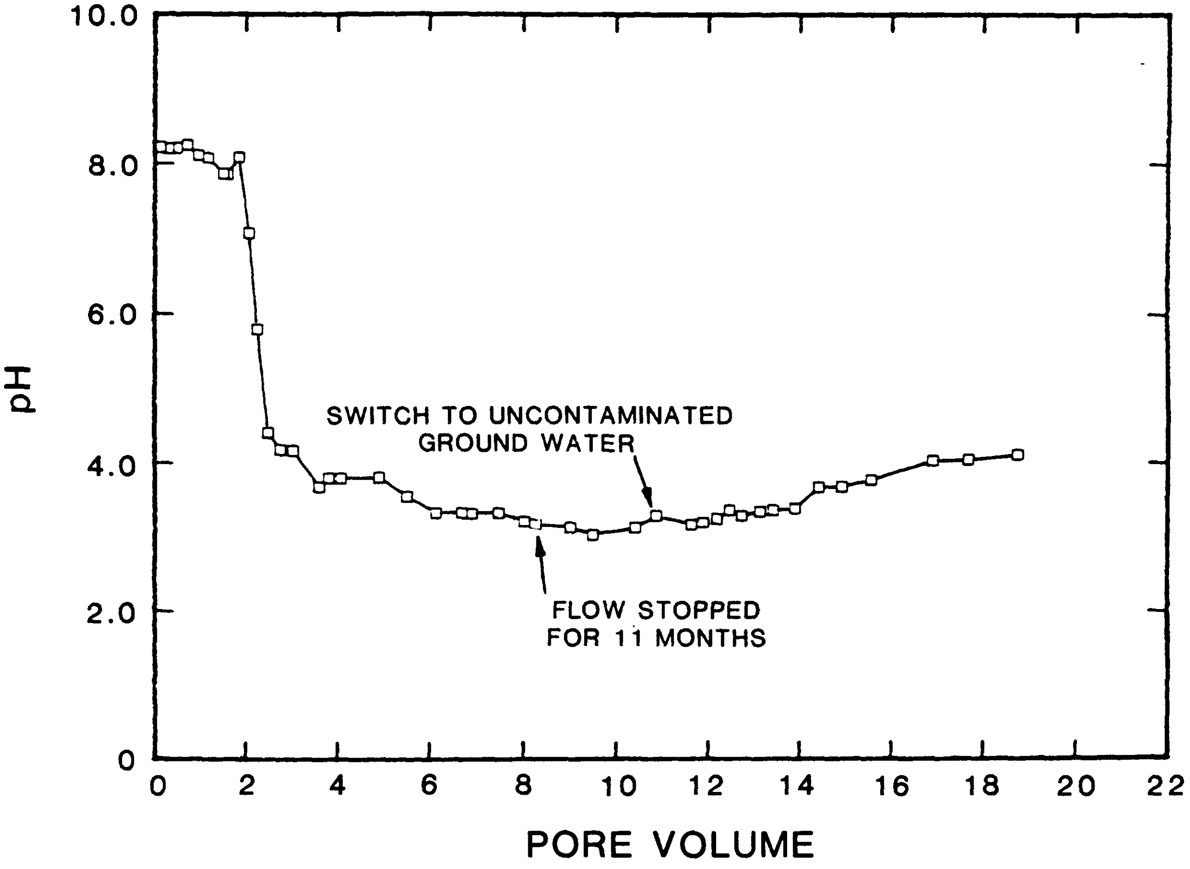

Figure D-7.—The effect of contaminated and uncontaminated ground water on effluent pH when passed through a laboratory column containing unconsolidated alluvium.

Uncontaminated ground water was introduced into the column near pore volume 11. Data between pore volumes 12 and 20 (fig. D–7) show only a slight increase in pH to a value of about 4; pH of the uncontaminated water is near 7. Thus, a source of H^+ has been formed in the alluvium preventing a rapid return of pH to background levels.

Breakthrough and rinse-out curves for the reaction of aluminum (Al), copper (Cu), and iron (Fe) with unconsolidated alluvium are given in figure D–8. Relative concentration is the concentration of a solute in the column effluent divided by the input concentration in the acidic ground water. Al, Cu, and Fe were completely removed from the first pore volume of acidic water. Precipitation of relatively insoluble Al, Cu, and Fe minerals at the existing high pH values (fig. D–7) are the likely mechanism. As pH decreases after the second pore volume, the solubility of Al, Cu, and Fe increases. Fe was the first solute to break through followed closely by Cu and, somewhat later, by Al.

Equilibration of acidic ground water with the alluvium for 11 months (fig. D–8, pore volume 8–9) resulted in a decrease in concentration for all three solutes, even though pH remained unchanged. This data indicated that the system does not attain complete equilibrium; the primary mechanism responsible for removing constituents from the acidic ground water is precipitation due to neutralization of H^+. This process occurs on the order of hours to days.

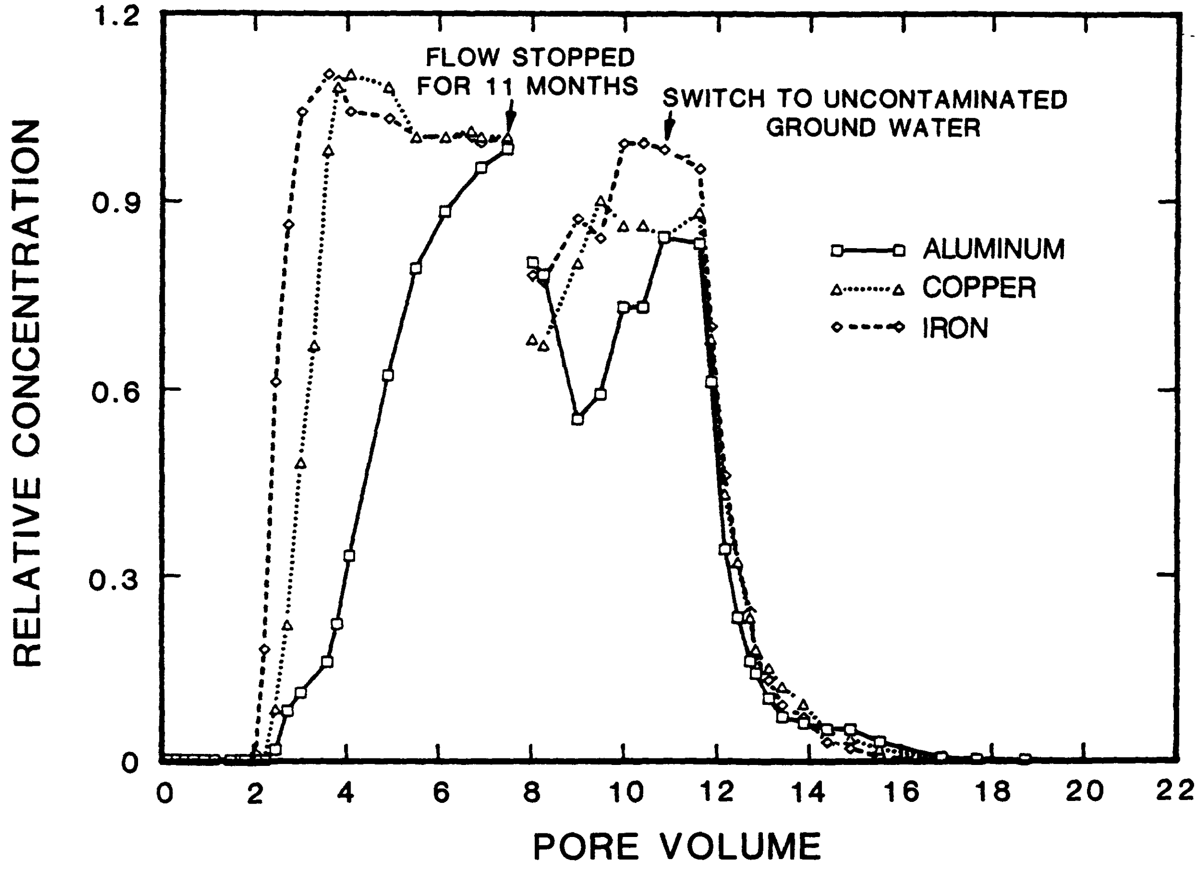

Figure D–8.—Breakthrough curves for aluminum, copper, and iron in acidic ground water flowing through unconsolidated alluvium.

After the acid ground-water source is removed, concentrations of Al, Cu, and Fe return to background levels within a few pore volumes, as the acidic water is displaced from the column (fig. D–8). The rapid decrease in the concentrations indicates the low solubility of their respective mineral phases.

Flow through carbonate cemented Gila Conglomerate significantly retards the transport of constituents in acidic ground water (fig. D–9). The pH remains high resulting in precipitation of Al, Cu, and Fe minerals. Al and Cu never appeared in the column effluents. The Fe increase starting at pore volume 5.5 is associated with a decrease in pH; however, flow was stopped before breakthrough was attained. Equilibration for 11 months resulted in higher pH values and complete removal of Fe.

Fe began to break through again just prior to the time when the influent was switched to uncontaminated ground water (fig. D–10). The rinse-out curve for Fe starts near pore volume 15. Fe was not removed from the column containing Gila Conglomerate as rapidly as it was from the unconsolidated alluvium. Also, Fe was still in the ferrous oxidation state. These occurrences are interpreted as dissolution of ferrous carbonate ($FeCO_3$) formed from reaction of Fe(II) in acidic ground water with calcium carbonate ($CaCO_3$) in the conglomerate.

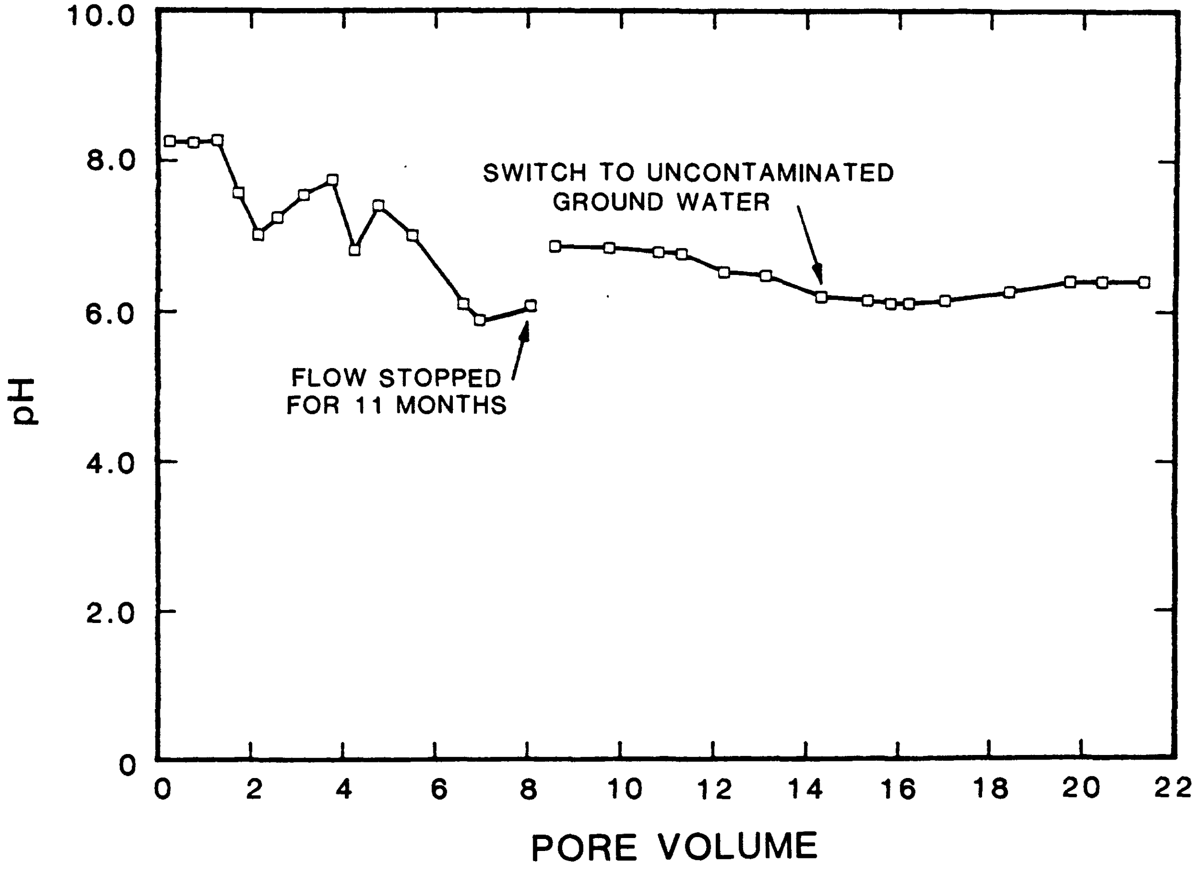

Figure D–9.—The effect of contaminated and uncontaminated ground water on effluent pH when passed through a laboratory column containing Gila Conglomerate.

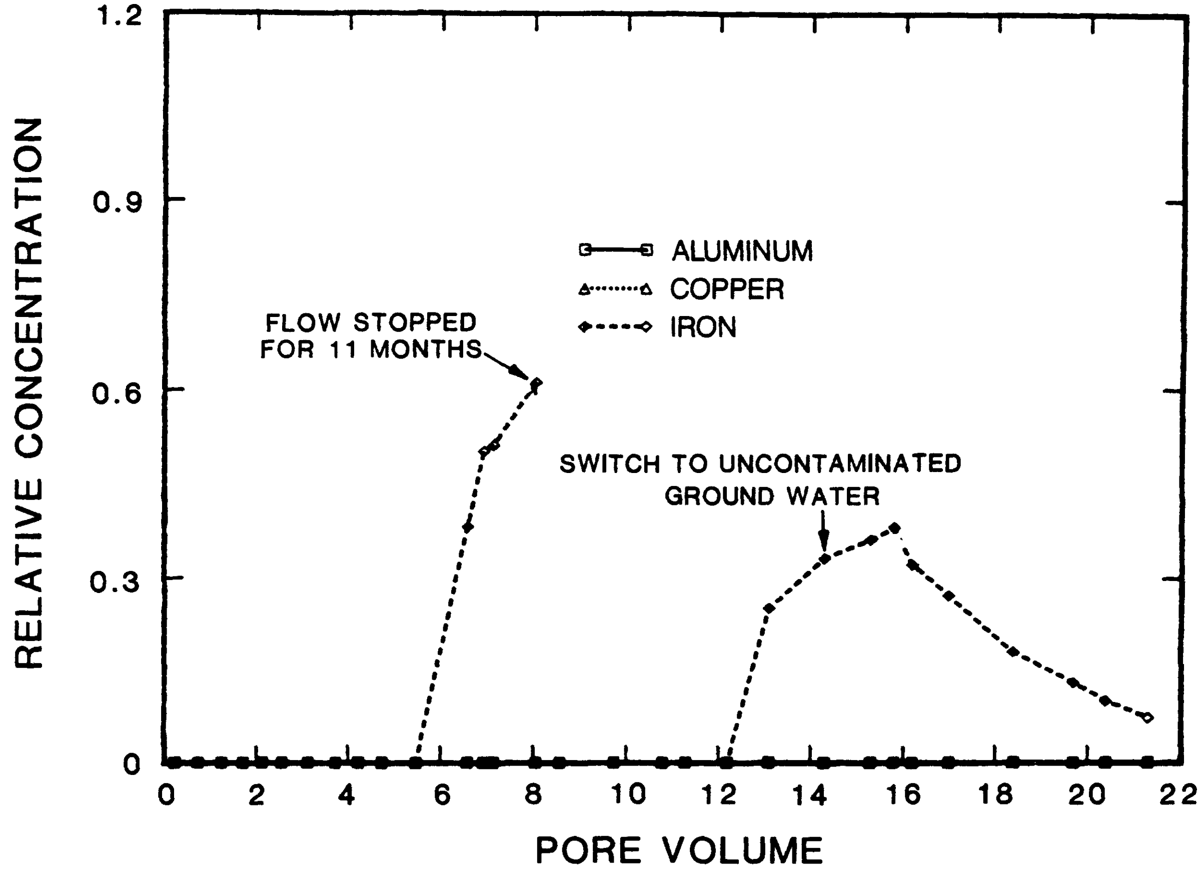

Figure D–10.—Breakthrough curves for aluminum, copper, and iron in acidic ground water flowing through Gila Conglomerate.

A summary of the mass of Al, Cu, and Fe removed from solution is given in table D–3, along with the mass of each element released from the alluvium and conglomerate to uncontaminated ground water. It is readily apparent that most of the Al, Cu, and Fe removed from solution is retained by the alluvium and conglomerate. Gila Conglomerate removed much more of each element than unconsolidated alluvium. The total capacity of the conglomerate for neutralizing acidic ground water has not yet been determined.

Table D–3.—*Comparison of the mass of aluminum, copper, and iron removed from acidic ground water with the mass released to uncontaminated ground water*

[Removed = micrograms removed from solution per gram of alluvium; released = micrograms released to solution per gram of alluvium]

	Unconsolidated alluvium		Gila Conglomerate	
Metal	Removed	Released	Removed	Released
Aluminum	280	23	1,040	0
Copper	87	16	561	0
Iron	1,220	268	8,820	824

In summary, the principal mechanism for removing constituents from the acidic ground-water plume is related to neutralization of H^+. A rise in pH causes the solubility of most metals to be exceeded and they precipitate. The unconsolidated alluvium, through which most of the plume is moving, has the capacity to neutralize approximately 1 to 2 pore volumes of acidic water. The much greater capacity of the Gila Conglomerate should greatly retard any movement of acidic water into the underlying aquifers of high quality water.

REFERENCE

Eychaner, J. H., and Stollenwerk, K. G., 1985, Neutralization of acidic ground water near Globe, Arizona: Proceedings of the American Water Resources Association Symposium on Ground-water Contamination and Reclamation, Tucson, Ariz., August 1985, p. 141–148.

DETECTION OF SELECTED PESTICIDES IN EXTRACTS OF CORE MATERIALS AND GROUND WATER FROM KANSAS

By T. R. Steinheimer[1]

Soil-core samples were taken from test plots on agronomy farms owned and operated by a university in Kansas. The samples were analyzed for residues of recently applied pesticides. Sampling was conducted by personnel of the U.S. Geological Survey using a truck-mounted, power-coring rig. Two core samples were collected on each test plot at five farms in November 1985. In March 1986, three farms were sampled a second time. At 1 farm, 10 core samples were taken at intervals throughout the stratum between land surface and the saturated zone. An associated ground-water sample also was collected at this site. Samples were collected through the root zone of each tilled plot to a depth of approximately 1.5 meters in soils characterized as loams and sandy loams. The study focused on distribution and biogeochemical breakdown of selected chemicals. The list of pesticides developed for the study was based upon information provided by agricultural engineers on site at each farm. Although this information was fragmented and incomplete with respect to date of application, formulations mixed or diluted, and estimated rates of application, it was sufficient to develop a list of nine analytes that were representative of the organic pesticides applied across Kansas during 1985 and 1986. As reflected by data of pesticide use nationwide, these chemicals are primarily weed-control agents. Among the herbicides, the list includes triazines, atrazine and cyanazine, with the triazine-like material, metribuzin. This list also includes the alpha-chloroacetanilides, alachlor and metolachlor, and the ortho-dinitroaniline material, trifluralin. One organophosphate insecticide, terbufos, is included, with two relatively new fumigant-fungicide agents, triadimefon and triadimenol.

Because of the lack of standardized multiresidue techniques for pesticide analyses in soils, several methods were examined that incorporate new approaches to preparation of an extract for instrumental analysis. One method uses solid-phase extraction carried out directly on an aqueous-methanol solution of air-dried soil. A second method uses methanol extraction on a mechanical shaker, followed by dilution in water and phase transfer into methylene chloride. Because several of the herbicides contain functional groups which render them weakly basic, a third method incorporates a pH adjustment of the soil sample just prior to extraction by methods previously described. Instrumental analysis for pesticide detections in soil-core extracts also was examined. High-resolution gas chromatography with detection by element-selective devices (sometimes referred to as "screening techniques") was determined to be unacceptable for multiresidue pesticide detections in soil cores. Core materials, with nonuniform surface chemistry and particle size, are difficult to extract for any divergent group of organic pollutants because of the larger number of coextracted chemical artifacts accompanying the pesticides. This situation greatly complicates interpretation of the chromatogram. Gas chromatography with mass analysis was necessary for unambiguous identifications and to avoid false positives.

Atrazine and alachlor were identified in the ground-water sample collected in November 1985, four months following the last application. Identifications were confirmed by ion-trap mass spectrometry (ITMS) with

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

concentrations for both herbicides less than 1 microgram per liter. No other pesticides were confirmed by ITMS in the soil-core extracts.

GASOLINE AND DIESEL-OIL CONTAMINATION OF GROUND WATER AT YAKIMA, WASHINGTON: SITE DESCRIPTION AND RESEARCH GOALS

By J. C. Ebbert[1]

The U.S. Geological Survey and the Oregon Graduate Center are conducting research at a site in Yakima, Wash., where ground water has become contaminated with gasoline and diesel oil. This study is part of the U.S. Geological Survey Toxic Waste—Ground-Water Contamination Program, which is a national thrust program to study the processes that affect the migration of toxic contaminants in ground water.

The objective of research at the Yakima site is to obtain a better understanding of the behavior of petroleum contaminants in the subsurface. Processes affecting the transport and decomposition of petroleum compounds in both the unsaturated and saturated zones are being investigated. This abstract describes the site and summarizes research activities that comprise the initial phase of study at the site.

Ground-water contamination at the Yakima site was first detected in 1980 when the owner of a downgradient domestic well reported the odor of gasoline in his well water. From 1980 through 1982, additional households reported contamination of domestic water supplies. The cause of the contamination was traced to leaks in improperly installed delivery lines at a service station on North First Street (fig. D-11). New tanks, were installed in June 1979, and the delivery lines were repaired in October 1982.

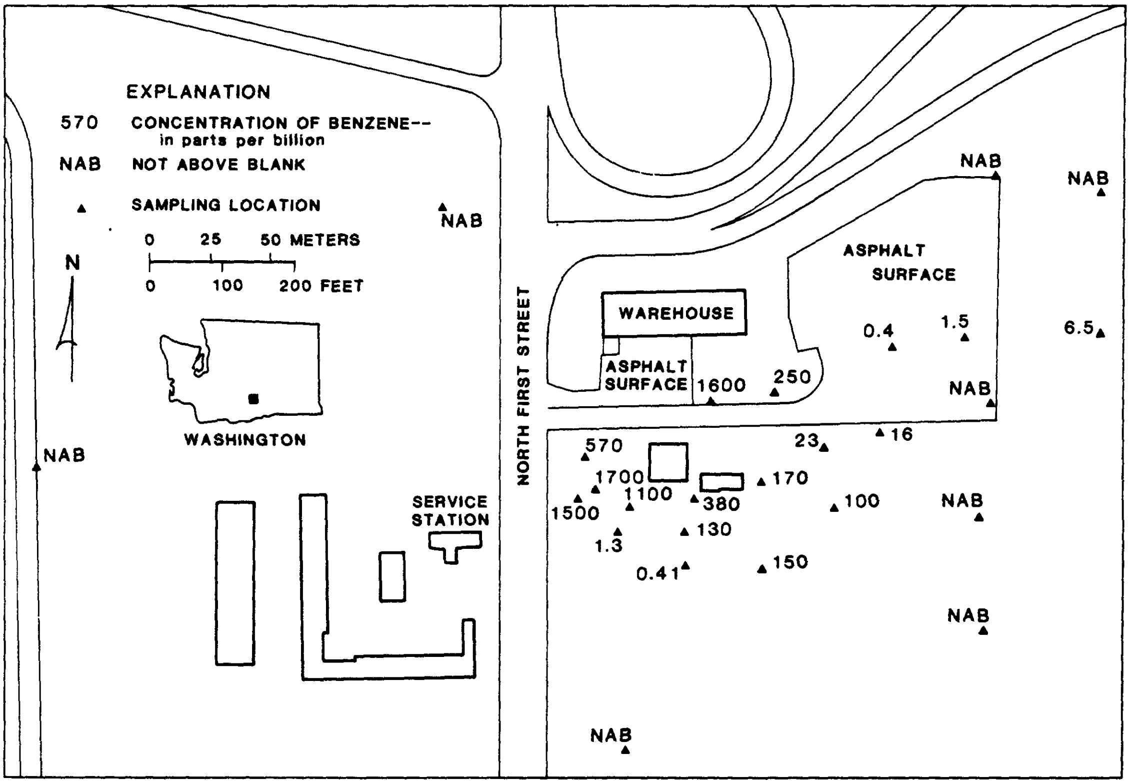

Figure D-11.—Location of sampling sites and concentrations of benzene in ground water sampled at the water table, November 1986.

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[1] U.S. Geological Survey, Tacoma, Wash.

The volume of product lost for the period from September 1981 through October 1982 was estimated from an audit of inventory records. The audit indicated a loss for the period of 22,500 L (liters) of leaded gasoline and 6,560 L of diesel oil, or an average combined loss of 2,070 L per month. Total product loss may have been as much as 83,000 L if the leakage occurred at the above rate for the entire 40-month period from the time of installation of the tanks and delivery lines to the time of repair.

Land use in the vicinity of the service station is mixed commercial, residential, and vacant. The service station lot as well as some of the adjacent and nearby properties are paved (fig. D-11). The presence of paved areas may affect the vapor-phase transport of volatile hydrocarbons in the unsaturated zone.

The study site lies on the alluvial plain of the Yakima River. Lithologic descriptions and preliminary sampling of wells at the site indicate that the contamination plume lies wholly within a unit of unconsolidated fluvial sands and gravels of Holocene age.

The direction of ground-water flow is generally eastward from the service station toward the Yakima River, which is approximately 900 m (meters) east of North First Street. The water table lies about 3.3 m beneath land surface, and annual fluctuations of the water table are about 1.3 m.

Gasoline and diesel oil are still present in sufficient amounts in the vicinity of the service station to be a significant source of dissolved hydrocarbons to the ground water (fig. D-11). Data from test wells and reports from owners of downgradient domestic wells indicate that there is temporal variability in downgradient contamination concentrations. Considering that the water table fluctuates seasonally at the site by as much as 1.3 m, the zone of contact between ground water and any remaining free product held at residual saturation also fluctuates. To better understand the process of dissolution of soluble hydrocarbons into the ground water, research at Yakima proposes to answer: (1) how do water-table fluctuations affect the vertical distribution and subsequent dissolution of free-product gasoline and diesel oil; and (2) in the zone of contact between free product and ground water, are the concentrations of petroleum hydrocarbons in ground water in equilibrium with respect to the free product, and if so, can the free product be considered an ideal solution for purposes of computing equilibrium concentrations?

The volatilization of hydrocarbons from free product to soil gas and then to the atmosphere in the unsaturated zone can be an important process for the removal of contaminants from the system. Also, the transport of oxygen in the opposite direction, from the atmosphere to the free product, can be important to the aerobic biologically mediated decomposition of contaminants (Hult and Grabbe, in press). Research at Yakima is being conducted to investigate the processes that control the transport of gaseous hydrocarbons and oxygen in the unsaturated zone and how gaseous transport is affected by paved surfaces.

Concentrations of lead in the sediments composing the aquifer indicate that gasoline-derived lead has migrated up to 230 m downgradient of the service station. However, dissolved-lead concentrations in ground water sampled at the same location as the aquifer material were low (about 1 microgram per liter). Therefore, the elevated concentrations of lead in aquifer material suggests that some of the lead once existed in a more mobile form than is indicated by the current distribution of lead between water and sediments. Research is being conducted at Yakima to investigate the processes that control the mobility and distribution of gasoline-derived lead in ground water.

REFERENCE

Hult, M. F., and Grabbe, R. R., in press, Distribution of gases and hydrocarbon vapors in the unsaturated zone, *in* Ragone, S. E., ed., U.S. Geological Survey Program on Toxic Waste—Ground-Water Contamination: Fiscal year 1986 program overview and selected abstracts from the Second Technical Meeting, Cape Cod, Mass., October 21–25, 1985: U.S. Geological Survey Open-File Report 86–481.

MOVEMENT AND FATE OF AGRICULTURAL CHEMICALS IN THE SURFACE AND SUBSURFACE ENVIRONMENTS AT THE PLAINS WATERSHED RESEARCH SITE, SOUTHWESTERN GEORGIA

By D. W. Hicks[1], J. B. McConnell[1], and L. E. Asmussen[2]

A growing concern in the United States is the potential for nonpoint ground-water contamination by agricultural chemicals. During 1984, the agricultural industry in this country used about $3x10^8$ kg (kilograms) of pesticides and over $1.0x10^{10}$ kg of nitrogen fertilizer. Little is known about the occurrence, movement, and fate of these widely used chemicals in the subsurface environment. Research programs are needed to: (1) develop procedures for estimating the potential for ground-water contamination by agricultural chemicals, (2) better understand the movement and fate of the chemicals in the subsurface, and (3) provide information necessary to develop alternative management practices to reduce or eliminate the occurrence of these chemicals in ground water. To address these needs, the Plains Watershed Research Investigation was initiated in 1984 by the U.S. Geological Survey and the Agricultural Research Service.

Major objectives of the study are to provide information of transfer value on the physical, chemical, and microbial processes that govern the transport and degradation of pesticides and nitrogen compounds in the crop-root zone, the unsaturated zone, and the saturated zone, and to develop a conceptual framework for applying the process-oriented findings. The experimental design of the study separates the hydrologic system into four components: (1) crop-root zone, (2) unsaturated zone, (3) saturated zone, and (4) stream system. Research categories include hydrologic system definition, simulation of flow and transport, controlled pesticide transport experiments, nitrogen cycling studies, microbial studies, and methods development. Each research activity is planned to concentrate on testing hypotheses that relate to the specific processes that affect the occurrence and movement of pesticides or nitrogen compounds, and that relate to simulation of the four components of the hydrologic system. Mathematical models that predict the movement of these compounds in the individual components of the hydrologic system are planned to be interfaced to obtain a simulation of overall conditions. Characterizations and quantifications of the physical, chemical, and microbiological processes are planned to be incorporated into each model segment so that the integrated model can be used to assess impacts of, and to manage, the agricultural chemicals that are of concern to the environment.

The study area is located in Sumter County, near Plains, Ga., in the Fall Line Hills district of the Coastal Plain physiographic province and encompases an area of about 650 ha (hectares). The watershed of Ty Ty Creek Tributary, which drains an area of about 270 ha, is included in the study area, and is typical of watersheds within the district. Approximately 160 ha of the watershed consist of arable land; the remainder is mostly pine and hardwood forest. Geohydrologic data indicate that the watershed recharges an important regional aquifer, creating the potential for surface-applied chemicals to pass through the 3.3 to 16 meters of unsaturated sandy or sandy-clay material and reach the aquifer. Agricultural chemicals of interest to this study include eight herbicides, two fungicides, and three nematicides.

[1] U.S. Geological Survey, Doraville, Ga.

[2] U.S. Department of Agriculture, Agricultural Research Service, Tifton, Ga.

CHAPTER E.—RESEARCH METHODS AND TECHNIQUES OF TOXIC WASTE—GROUND-WATER CONTAMINATION PROGRAM

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CHAPTER E.—RESEARCH METHODS AND TECHNIQUES OF TOXIC WASTE—GROUND-WATER CONTAMINATION PROGRAM

INTRODUCTION

By Bernard J. Franks[1]

A significant part of the investigative effort of the Toxic-Waste—Ground Water Contamination Program involves development of research methods and techniques necessary to study contaminated ground-water systems. This chapter presents results of some of this research, from field comparisons of sampling devices through regional reconnaissance appraisals of ground-water quality.

Field comparisons of sampling devices are discussed by Imbrigiotta and others, and by Sonntag. The former article compares data using five different downhole samplers to collect purgeable compounds, noting that significant differences between sampling devices were not consistent either among sites or compounds detected at each site. Sonntag evaluates a prototype, stainless steel downhole sampler, capable of maintaining downhole isobaric conditions. He also observed no significant difference between sampling methods in analyses of purgeable organic compounds.

The paper by Reilly reviews advection and dispersion, the two physical mechanisms that influence the movement of solutes in the ground-water system. He emphasizes that ground-water systems are three-dimensional and heterogeneous.

Thorn presents applications of carbon-13 Fourier transform nuclear magnetic resonance (C–13 NMR) spectroscopy in analyzing complex mixtures of organic compounds in the subsurface. He suggests C–13 NMR can complement more traditional methods in the analysis of such mixtures.

Adsorption of selenium by iron and manganese oxides is discussed by Balistrieri and Chao. They investigated the role of pH, iron and manganese oxides, and solution composition in chemical speciation and mobility of selenium in the environment.

The distribution of arsenic and heavy metals in an alluvial aquifer in western Montana is discussed by Ficklin and Moore. They conclude that arsenic was originally adsorbed on iron and manganese hydroxides; reduction to ferrous iron and soluble As(III) occurred as a result of burial and precipitation of available arsenious sulfide or arsenopyrite.

Cain and others conclude this chapter by summarizing reconnaissance appraisals of anthropogenic effects on regional ground-water quality. Nationwide, 14 areas are part of this attempt to quantify the effects of land use on ground-water quality. Preliminary results of appraisals in eight of these areas are summarized.

All the papers referred to above appear in Chapter E of this report: U.S. Geological Survey Open-File Report 87–109, entitled, "U.S. Geological Survey program on Toxic Waste—Ground-Water Contamination: Proceedings of the third technical meeting, Pensacola, Florida, March 23–27, 1987."

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[1] U.S. Geological Survey, Tallahassee, Fla.

FIELD COMPARISON OF DOWNHOLE AND SURFACE SAMPLING DEVICES FOR PURGEABLE ORGANIC COMPOUNDS IN GROUND WATER

By Thomas E. Imbrigiotta[1], Jacob Gibs[1], James F. Pankow[2], and
Michael E. Rosen[2]

Significant losses of purgeable organic compounds (POC) can occur when conventional procedures for collecting a sample from a well are used. The current standard procedure involves pumping or bailing a sample to the surface, placing it in a 40-milliliter glass vial, and sealing the vial with a Teflon[3]-lined septum cap. Volatile components of the sample can: (1) degas while the sample is being raised to the surface due to pressure and temperature changes, (2) volatilize while the vials are being filled due to aeration, and (3) be lost through leaking vial seals or sorption by the porous Teflon-lined septum. To attempt to minimize these problems, sampling devices have been developed to take samples downhole. Downhole samplers either isolate and concentrate the compounds of interest from a well water sample or seal off a sample at the *in situ* pressure and temperature present at depth in the well. The samples are collected directly into containers that can be shipped to a laboratory for analysis, which minimizes sample handling. This field study compares the performance of a downhole isobaric sampler developed by the U.S. Geological Survey, a downhole adsorption/thermal desorption (ATD) sampler developed at the Oregon Graduate Center, a helical-rotor submersible pump, a surface ATD sampler, and a point-source bailer.

Three wells that contained a total of 12 POC detectable at concentrations from 0.5 μg/L (microgram per liter) to approximately 400 μg/L, were chosen for this field experiment. The first well was screened in a confined sand-and-gravel aquifer and the second and third wells were screened in unconfined sand-and-gravel aquifers. The three wells had depths to water of 17 m (meters), 10 m, and 4 m, respectively. Samples were collected in all wells at approximately 17 m below the top of the water column.

At each site, the well was flushed and temperature, pH, dissolved oxygen, specific conductance, absorbance at 254 nanometers, and chloride were monitored. When these measurements achieved stability, 8 to 10 replicate samples were collected with each sampler according to a protocol that eliminated any sampling order bias. The surface and downhole ATD samples were analyzed at the Oregon Graduate Center using a cryofocused capillary column gas chromatograph with a mass spectrometer detector. All other samples were analyzed at the U.S. Geological Survey laboratory in New Jersey using a purge and trap concentrator and a wide-bore capillary gas chromatograph with a photoionization detector and a Hall detector in series. Any interlab biases identified statistically were eliminated by standardization of the data. All results were compared using analysis-of-variance testing to determine if the sampling devices differed significantly, at the 95-percent confidence level, in their recovery of each POC.

Although significant differences in concentrations of POC were found between sampling devices at each of the three sites, considerable overlap of the sampler groupings were observed. Additionally, the order of samplers

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[1] U.S. Geological Survey, West Trenton, N.J.

[2] Oregon Graduate Center, Beaverton, Ore.

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

from most-effective to least-effective recovery varied among sites and among the compounds detected at each site. Overall, the POC concentrations recovered by the helical-rotor submersible pump, the downhole isobaric sampler, and the surface and downhole ATD samplers were not significantly different. The point-source bailer recovered somewhat lower POC concentrations.

The downhole isobaric sampler and the downhole and surface ATD samplers were found to have slightly lower coefficients of variation than the helical-rotor submersible pump and the point-source bailer. Thus, one apparent advantage of these sampling devices is an increase in precision that is probably due to fewer sample handling steps prior to analysis.

COMPARATIVE TEST OF TWO SAMPLING DEVICES FOR OBTAINING PURGEABLE ORGANIC COMPOUNDS FROM GROUND-WATER WELLS

By Wayne H. Sonntag[1]

A prototype downhole sampler for sampling purgeable organic compounds in ground water has been developed for use in small-diameter (as small as 38 mm (millimeter)) wells. The prototype sampler consists of a hollow stainless-steel cylinder, a stainless-steel moving center shaft, a stainless-steel fixed top piston with two Viton[2] o-rings, and a moving Teflon bottom piston with one Viton o-ring. The sampler was designed to be used with an existing small-diameter logging tool available from the U.S. Geological Survey, Borehole Geophysical Services Unit, in Denver, Colo. Using the logging tool with a winch, the sampler in either an open or closed position is lowered into the well to a prescribed depth. In the closed position, the sampler can be prefilled with distilled water and then opened at the prescribed depth. This prevents the inside of the sampler from contacting debris or oil which might be floating on the water surface in the well. In the open position, because the sampler is of a "flow-through" design, the well can be pumped with the sampler in place using either a submersible pump above the sampler or a conventional pump at the surface. The "flow-through" design allows the sampler to be flushed with water of the same chemical composition as the sample, thereby reducing any alteration of the sample. It also allows the user to determine at what time and, concurrently, at what volume of water pumped from the aquifer to take the sample.

To obtain a water sample, the sampler is closed using an electric motor contained in the logging unit. It is then returned to the surface and placed in a holder for sample withdrawal. To facilitate the removal of the sample from the sampler, a circular septum through-fitting which holds a 14-mm septum has been incorporated into the wall of the sampler. A needle and syringe assembly, equipped with a two-way microvalve, is inserted through the circular septum. The moving bottom piston is then pushed up the sampler cylinder bore, displacing the sample water into the syringe. When the syringe is filled, the microvalve is closed, and the entire syringe assembly is sent to the laboratory.

The major advantages of this system are: (1) samples of water are withdrawn directly into a gas chromatography syringe which can be used in the laboratory; (2) exposure of the sample to pressure changes, with the potential loss of purgeable compounds, is eliminated in both the field and the laboratory; and (3) the possibility of field personnel encountering a potentially hazardous substance is minimized.

A comparative test of the prototype sampler and a double-ball Teflon bailer was conducted on May 15, 1986, to evaluate the effectiveness of the prototype sampler. The test was conducted at an existing well (U.S. Geological Survey well G-3329) located at the Miami International Airport, Miami, Fla. Well G-3329 is a 15-cm (centimeter) diameter well, drilled to 18 m (meters) below land surface. It is cased to 17.3 m below land surface with polyvinyl chloride (PVC), and is finished open hole between 17.3 m and 18 m below land surface. This well was selected for this test because: (1) its large diameter permitted both samplers to be lowered into the well

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[1] U.S. Geological Survey, Miami, Fla.

[2] Use of brand names in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

simultaneously; and (2) samples of water for purgeable organic compounds have been collected for several years from a companion well located adjacent to well G–3329 by Dade County's Department of Environmental Resources Management (DERM).

Prior to sampling, five well casing volumes of water were pumped from the well. Field determinations of pH, specific conductance, and temperature were made after one and five casing volumes had been pumped from the well to verify that native ground water was being sampled. After pumping was completed, both samplers were lowered into the well simultaneously at a rate of approximately 0.6 m/s (meter per second), to 0.6 m above the top of the open-hole interval. This procedure was repeated three times. The samplers were fastened to one another, using cleaned stainless-steel wire, to ensure that the intakes of both samplers were positioned together. During the fourth and fifth repetitive samplings, the prototype sampler was lowered to the same depth as before. However, the bailer was lowered to 1.6 m below the water surface in the well. This was done to duplicate field procedures presently used by various State and local agencies to sample for purgeable organic compounds in ground water.

Upon retrieval of the two samplers, samples of water were obtained from the bailer by overflowing 40 mL (milliliter) septum vials from the bottom of the vials. This method was used to minimize exposure of the sample water to the atmosphere and reduce agitation of the sample water. Samples of water were withdrawn from the prototype sampler using gas chromatography syringes and needles to penetrate the inert septum of the sampler. The syringes were equipped with gas-tight valves to seal the sample in the syringe. In addition to the five replicate samples obtained from each sampler, several duplicate samples (subsamples) were taken from the prototype sampler. A field blank of the distilled water, used to rinse both samplers, was also collected and analyzed for purgeable organics. After the samples were collected, the samples were chilled and transported the same day to the University of Miami's School of Medicine, Division of Chemical Epidemiology Laboratory. All samples were analyzed within 5 days of collection using a Tracor Model 222 gas chromatograph and Hall detector.

Results of the analyses for purgeable organics from each sampler are shown in table E–1. The samples are listed sequentially from 1 to 5 along with the approximate time of sampling. Duplicate samples (subsamples) are designated by a "D" after the sequence number. Data collected by DERM from the companion well adjacent to well G–3329 is also shown in table E–1. Samples of water were collected from this well by DERM, 1.6 m below the water surface, using a double-ball Teflon bailer.

A one-way analysis of variance was performed on the comparative test data for cis-1,2-dichloroethene, chlorobenzene, p-dichlorobenzene, and o-dichlorobenzene to test if the observed differences among the sample means of the two samplers were significantly different. A significance level of α=0.05 was used. No analysis of variance was performed on the data for 1,1-dichloroethane due to limited amount of values above detection limits. Based on the results of the analysis of variance, it appears that the means of the two samplers for the four purgeable organics considered were not significantly different. In addition, visual inspection of the data collected using the bailer shows no significant difference between the samples of water collected at 0.6 m above the top of the open-hole interval (14.6 m below the water surface) and samples of water collected at 1.6 m below the water surface. It, therefore, appears that the prototype sampler and the bailer were equally effective in collecting samples of water for the analysis of purgeable organic compounds.

Table E-1.—*Purgeable organic data for well G-3329 and a companion well, Miami International Airport, Miami, Florida*

[Concentrations shown in micrograms per liter; BDL, below detection limits of 1.0 microgram per liter; SD, standard deviation]

Sample sequence number	Time	1,1-Dichloro-ethane	cis-1,2-Dichloro-ethene	Chloro-benzene	p-Dichloro-benzene	o-Dichloro-benzene
Teflon bailer						
1	1020	1.4	3.4	293	17.0	29.5
2	1123	BDL	2.4	278	14.2	32.9
3	1200	BDL	2.3	273	14.2	34.4
4	1330	BDL	1.9	302	13.6	34.1
5	1410	BDL	2.0	294	14.2	35.6
Mean	—	—	2.4	288	14.6	33.3
SD	—	—	.6	12	1.3	2.3
Prototype sampler						
1	1020	BDL	4.4	230	15.5	32.0
2	1135	1.0	2.8	264	15.6	32.0
2D	1135	BDL	2.6	308	15.4	38.4
3	1210	BDL	2.6	302	14.2	34.4
4	1340	BDL	2.6	292	13.2	34.1
5	1415	BDL	2.7	294	15.4	35.3
5D	1420	1.0	3.0	302	14.2	33.6
Mean	—	—	3.0	285	14.8	34.3
SD	—	—	.6	28	0.9	2.2
Blank	—	BDL	BDL	BDL	BDL	BDL
DERM sampling of companion well, November 1985 through June 1986						
—	Nov	2.6	6.6	30	14.2	30.1
—	Dec	1.0	5.9	206	19.8	29.7
—	Jan	BDL	6.0	210	21.3	37.1
—	Feb	BDL	2.8	160	10.7	20.8
—	Mar	BDL	3.9	217	14.8	28.4
—	Apr	—	—	—	—	—
—	May	BDL	2.0	209	12.5	38.2
—	June	BDL	2.1	128	7.7	20.5

CONSIDERATION OF THE FLOW SYSTEM IN COLLECTION AND INTERPRETATION OF GROUND-WATER QUALITY SAMPLES

By Thomas E. Reilly[1]

In recent years, both the Federal and Cooperative Programs of the Water Resources Division, U.S. Geological Survey, have reflected the importance of ground-water contamination. Significant resources are allocated under these programs for the study of the problems related to the movement of contaminants in ground-water systems. The approach of many of these studies is to infer the effect of various sources of contamination by sampling ground water. In order for this approach to be of any value, the physical mechanisms that move the ground water and associated solutes must be understood and included in the interpretive analysis.

Ground-water systems are three dimensional and heterogeneous. Water samples obtained from wells have to be considered in the context of the three-dimensional flow system and the source of water being sampled. Only in the context of where the water came from and the time of travel from the source can a technically sound interpretation of the water-quality data be made.

The two physical mechanisms that influence the movement of solutes in the ground-water system are advection and dispersion. These two mechanisms as commonly perceived, however, are not independent.

Advection is the process by which solutes are transported by the bulk motion of the flowing ground water. The bulk motion of flowing constant-density ground water is characterized by the average linear velocity (v) which is defined as:

$$v = \frac{K}{n}\frac{dh}{dl} \tag{1}$$

where:

K = hydraulic conductivity (L/T),
n = porosity (dimensionless),
h = hydraulic head (L), and
l = distance along a flowline (L).

The hydraulic conductivity and porosity can and usually do vary significantly in three dimensions in natural ground-water systems. The values of these parameters that are used to make any calculation of the average linear velocity will be dependent on the size of the volume of aquifer over which these parameters are averaged or approximated.

Another physical mechanism (or psuedomechanism) called mechanical dispersion is then introduced to account for variations in movement that are not accounted for by the average advective movement. Mechanical dispersion is an attempt to account for variations in velocity of a solute resulting from pore-scale effects and unknown variations in hydraulic conductivity and porosity.

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[1] U.S. Geological Survey, Reston, Va.

When a well is sampled, the scientist analyzing the data must evaluate the effects that advection and dispersion had on the water arriving at the well. Samples from wells that are pumped infrequently represent the quality of water from sources governed by natural processes. Short well screens give a clear picture as to the concentrations at one point in the three-dimensional system, whereas long well screens can mix waters of various qualities. Frequently pumped wells, such as public supply wells, alter natural flow paths. Ground-water flow systems respond very differently to stresses depending upon their boundary conditions, storage properties, and transmitting properties in relation to the degree and location of the stresses.

Inductive reasoning must be used to draw conclusions about the general source of contamination from some particular water samples obtained at a well (or wells). However, the physical processes of advection and dispersion greatly affect the path and time of movement of a contaminant. Without understanding the three-dimensionality of the flow system and the paths and rates of movement within this three-dimensional continuum, any inductive conclusions are doomed to failure.

THE USE OF CARBON-13 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY IN THE ANALYSIS OF COMPLEX SAMPLES OF ENVIRONMENTAL INTEREST

By Kevin A. Thorn[1]

Solution state Carbon-13 (C-13) Fourier transform nuclear magnetic resonance (NMR) spectroscopy has been a routine method for the structural determination of organic compounds since the early 1970's. As high field NMR spectrometers (magnetic field strengths of 4.7 to 11.7 tesla, corresponding to proton resonant frequencies of 200 to 500 MHz (megahertz)) become more accessible to environmental scientists, C-13 NMR is being used increasingly for the structural analysis of complex mixtures of organic compounds of environmental significance. The proliferation of research over the last 7 years in the application of C-13 NMR to the study of humic substances is testimony to this. This presentation: (1) describes the types of analytical problems which are appropriately addressed through C-13 NMR, (2) discusses the general protocol for analysis of complex samples by NMR, and (3) presents two examples of how C-13 NMR was used very successfully at U.S. Geological Survey hazardous waste research sites. These include the analysis of biodegraded crude oil fractions from the Bemidji, Minn., site, and the analysis of detergents from ground water at the Cape Cod, Mass., site.

C-13 NMR can complement or in some instances supplant gas chromatography/mass spectrometry (GC/MS) in the analysis of complex mixtures of organic compounds. C-13 NMR is an appropriate technique when:

- Analysis of a whole sample is required before chromatographic separation, chemical degradation, or chemical derivatization is performed;
- Analysis of subfractions of a whole sample is required to monitor the progress of chromatographic separations, chemical degradations, or chemical derivatizations;
- The sample cannot be chromatographically separated into pure components;
- The sample is not amenable to GC/MS, for example, because the individual molecules in the sample are of too high a molecular weight to pass through a GC column; or
- Very little is known about the general structural characteristics of the sample.

NMR spectroscopy is a nondestructive technique; samples can be completely recovered after the spectra are recorded. For this reason, NMR is often the the first step in the analytical scheme for the analysis of a complex mixture of organic compounds.

After finding a suitable deuterated solvent for the sample of interest, the typical NMR analysis of a complex mixture proceeds as follows:

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

1. A nonquantitative C-13 NMR spectrum is obtained under conditions which maximize signal to noise to determine what types of carbon nuclei are present in the sample, for example aliphatic carbons, carbons bonded to heteroatoms, aromatic carbons, carbonyl carbons, and so forth.

2. The spin lattice relaxation times (T_1's) of the carbon nuclei are measured.

3. The quantitative distribution of carbon types present in the sample is determined by recording a quantitative C-13 NMR. This is accomplished by acquiring the NMR using inverse gated decoupling (to eliminate nuclear Overhauser enhancement) and pulse delays on the order of five times the longest T_1 present in the sample (to eliminate differential saturation effects).

4. An appropriate carbon multiplicity sorting experiment is performed. This includes both one-dimensional and two-dimensional experiments, such as attached proton test (APT), distortionless enhancement by polarization transfer (DEPT), and heteronuclear two-dimensional J-resolved (HET2DJ) spectroscopy. These experiments differentiate among methyl, methylene, methine, quaternary, protonated aromatic/olefinic, non-protonated aromatic/olefinic, and carbonyl carbons.

5. If more detailed information on the hydroxyl group functionality of the sample is necessary, it can be obtained by recording C-13 NMR spectra of the sample after methylation with C-13 enriched reagents.

Aiken and others (Chapter C, this report) isolated hydrophobic and hydrophilic acid fractions from ground water downgradient of the oil pool at the Bemidji site. The acid fractions were presumed to be the partial biodegradation products of the crude oil. Before any attempt was made to identify individual components in the acid fractions by GC/MS, the hydrophobic and hydrophilic acid fractions were subjected to C-13 NMR analyses. Figure E-1 shows quantitative C-13 NMR spectra of the original crude oil from well 301 and the hydrophilic acid fraction from well 530. From the spectrum of the crude oil, the aliphatic carbons (10-55 ppm (parts per million)) are calculated to comprise 85 percent and the aromatic carbons (115-150 ppm) 15 percent of the carbons present in the sample. Even though crude oil is an extremely complex mixture, one can still observe in the spectrum discrete sharp line resonances representing individual carbon nuclei. The spectrum of the hydrophilic acid, however, exhibits very broad resonances, indicating that this fraction of organic acids is an order of magnitude greater in complexity than the original crude oil. Furthermore, this spectrum in combination with the APT spectrum (not shown) indicates that carboxyl carbons (160-180 ppm) comprise 23 percent, aromatic carbons (90-160 ppm) 11 percent, secondary hydroxyl carbons (60-90 ppm) 18 percent, and C-aliphatic carbons (0-60 ppm) 48 percent, of the total carbons in the mixture. With the information obtained on the oxygen containing functional groups, an appropriate derivation procedure for analysis of the hydrophilic acid fraction by GC/MS could be chosen.

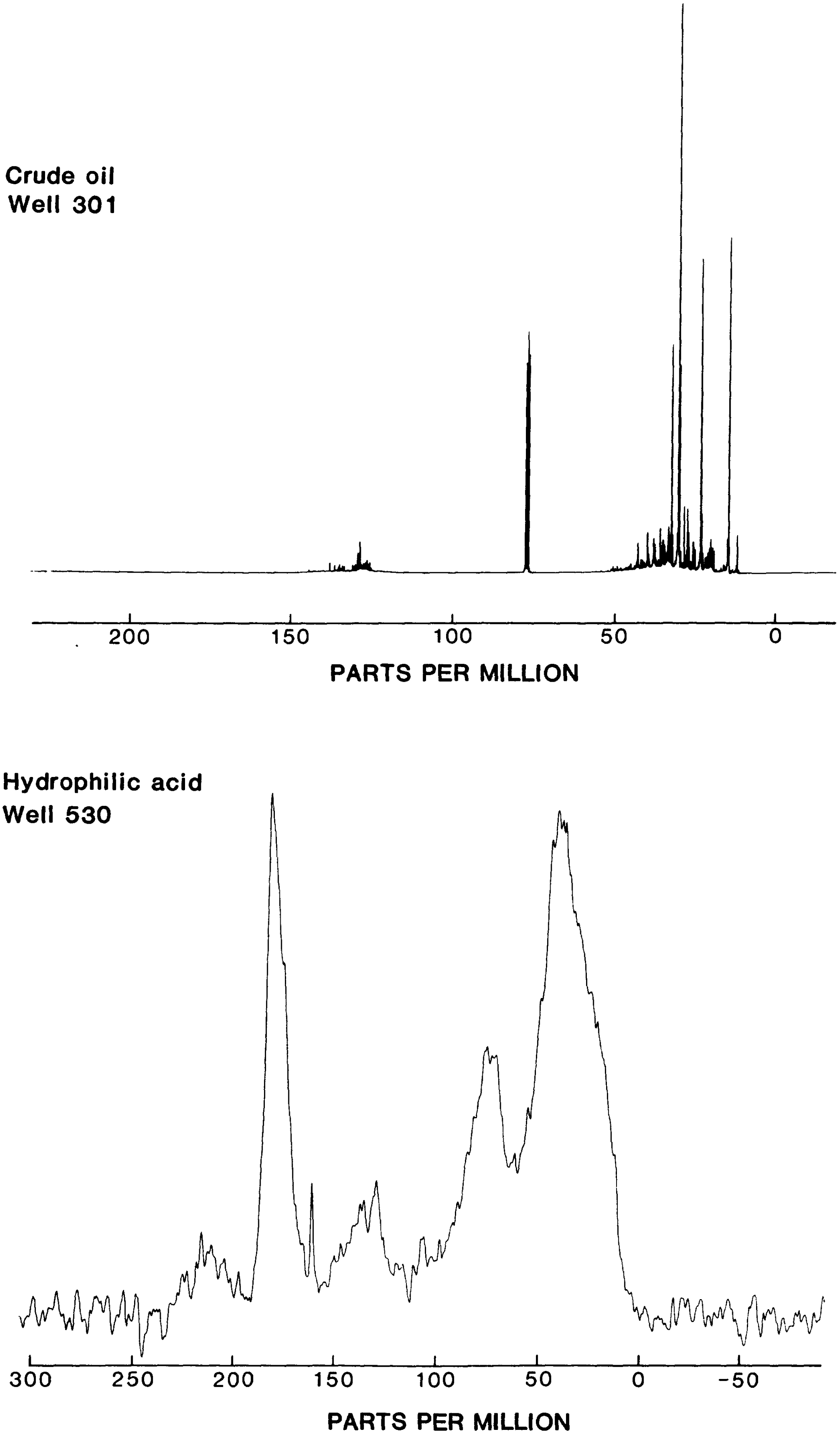

Figure E-1.—Quantitative carbon-13 nuclear magnetic resonance (C-13 NMR) spectra of crude oil and hydrophilic acid.

In researching the contamination of ground water by anionic detergents at the Cape Cod site, Thurman and others (1986) hypothesized that detergents formed two distinct plumes downgradient from sewage disposal beds at Otis Air Base. The furthest downfield plume at 3.5 km (kilometers) was assumed to consist of alkyl benzene sulfonate (ABS) detergents, and the upfield plume at 0.6 km to consist primarily of linear alkylbenzene sulfonate (LAS) detergents. Structural representations of ABS and LAS detergents are presented in figure E–2. In order to test this hypothesis, the anionic detergent fractions were isolated from wells at these plumes using XAD[2] resins (Thurman and others, in press). The most common technique for analysis of these detergents is to perform a desulfonation of the surfactant to an oil, and then identify the hydrocarbon structures via GC/MS. Unfortunately, this technique was found to be incapable of distinguishing ABS from LAS. APT C–13 NMR spectra of ABS standard, LAS standard, and the detergent fraction isolated from the 3.5 km downfield plume are presented in figure E–2. In APT spectra, methyl and methine carbon resonances are negative, methylene and quaternary carbons positive. The C–13 NMR spectra clearly distinguish the ABS standard from the LAS standard. The alkyl chains of ABS are highly branched compared to LAS. The APT spectrum of the detergent isolated from the downfield plume is identical to the APT spectrum of the ABS standard. Thus, C–13 NMR unequivocally identified the anionic surfactant isolated from the 3.5 km downfield plume as ABS detergent.

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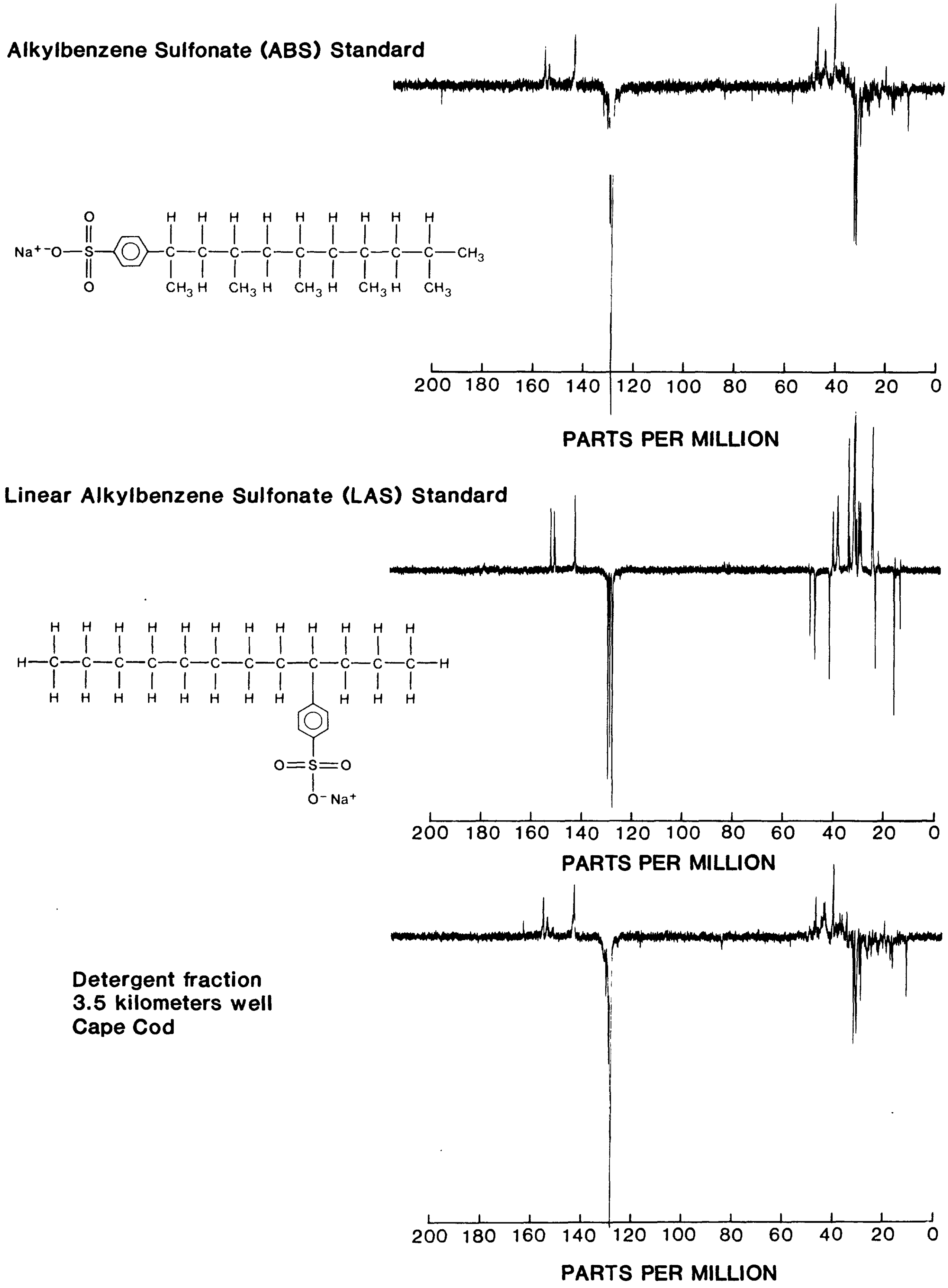
[2] The use of trademarks in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.



Alkylbenzene Sulfonate (ABS) Standard

Linear Alkylbenzene Sulfonate (LAS) Standard

Detergent fraction 3.5 kilometers well Cape Cod

Figure E-2.—Attached proton test carbon-13 nuclear magnetic resonance (C-13 NMR) spectra.

ADSORPTION OF SELENIUM BY IRON AND MANGANESE OXIDES: ENVIRONMENTAL IMPLICATIONS

By Laurie S. Balistrieri[1] and T. T. Chao[1]

The mobility, transport, and availability of toxic elements in the environment depend on the pH and redox conditions of the system, the chemical speciation of the elements, their adsorption and precipitation behavior, and their involvement in biological processes. Our general research focuses on the process of adsorption. Our approach is to manipulate variables, such as pH, oxide mineral type, or solution composition, in order to understand how they influence the adsorption behavior of an element.

In this research we examined the adsorption of selenium by goethite ($\alpha FeOOH$) and by disordered birnessite (δMnO_2). At low concentrations selenium is an essential element for animal nutrition, but at high concentrations it is toxic. Selenium can exist in four possible oxidation states: selenide (Se^{2-}), elemental selenium (Se^0), selenite (SeO_3^{2-}), and selenate (SeO_4^{2-}). Its chemical speciation and, therefore, behavior are highly dependent on the pH and pE of the environment. Iron and manganese oxides are common components of soils and sediments and play a major role in scavenging and accumulating certain elements. The affinity of selenium and the influence of pH (4–11), particle concentration (3–300 milligrams per liter), selenium concentration ($0.2\text{–}5\times10^{-6}$ Molar), competing anion concentration ((anion)/(Se)=0.25–50,000), and oxidation state (Se(IV) and Se(VI)) on the adsorption of selenium were compared for the two metal oxides. The data for the oxides indicate that: (1) the adsorption of selenite (Se(IV)) is characteristic of anion adsorption in that it increases with decreasing pH; (2) selenite adsorption at a given pH increases with increasing particle concentration; (3) the adsorption edge (that is, the pH range where adsorption goes from 0 to 100 percent) for selenite shifts to lower pH values with increasing total selenium concentrations; (4) the influence of anions, such as silicate, citrate, molybdate, oxalate, sulfate, and fluoride, on selenite adsorption depends on the relative affinity of the ions for the oxide surface and their relative concentrations; and (5) selenite adsorbs much more strongly than selenate (SeVI). The comparison of the data sets for the two oxides indicates that the affinity of selenite for goethite is slightly greater than that for δMnO_2. In addition, the shift in the selenite adsorption edge occurs at lower total selenium concentrations for goethite than for δMnO_2. This indicates a larger population of higher energy sites on the surface of δMnO_2 than on goethite.

Adsorption of selenite from systems containing goethite and δMnO_2 in various proportions was also examined. Preliminary results suggest that goethite appears to play a more important role in selenite removal in the mixed oxide systems than would have been expected based on the data from the individual systems.

On the basis of our observations, the environmental conditions which would tend to enhance the mobility of selenium with respect to adsorption are:

- Alkaline pH conditions in the soil, sediment, or ground water;
- High total selenium concentrations;

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

- The presence of high concentrations of additional anions which strongly adsorb and compete with selenium for surface sites; and
- Oxidizing conditions which encourage the presence of selenate over selenite.

THE DISTRIBUTION OF ARSENIC AND HEAVY METALS IN A CONTAMINATED ALLUVIAL AQUIFER, MILLTOWN, MONTANA

By Walter H. Ficklin[1] and Johnnie N. Moore[2]

The sediment of a reservoir on the Clark Fork River in western Montana is contaminated with arsenic and heavy metals. The sediment is the source of ground-water contamination in the adjacent alluvial aquifer (Woessner and others, 1984). The abundance of arsenic and heavy metals provides an opportunity to study the chemical reactions that occur when conditions change from oxidizing to reducing. When the reactions are known, control of the contamination should be more feasible.

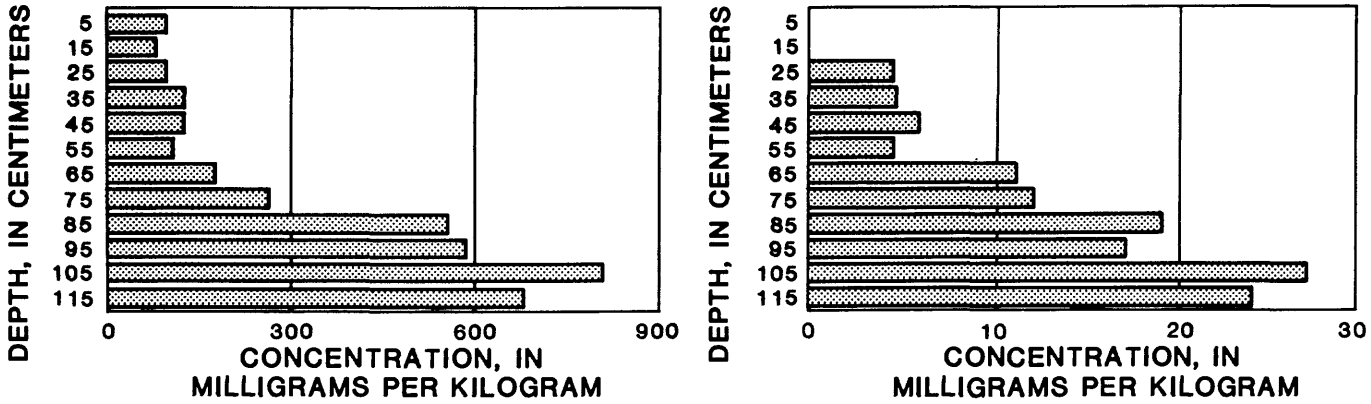
The concentration of metals in the interstitial water is controlled by iron and manganese oxyhydroxides in the oxidized zone and by precipitation as sulfides in the reduced zone. The change from oxidizing to reducing conditions also affects the concentration and oxidation state of arsenic. The arsenic occurs primarily as As(V) in the oxidized zone and As(III) in the reduced zone. The oxidizing-reducing interface of a 115-cm (centimeter) core sampled at 10-cm intervals occurs at about 50 to 60 cm and was determined by measurement of the redox potential using a platinum electrode, by measurement of dissolved oxygen, and by measurement of the concentration of ferrous iron in the water.

Some interesting trends are observed for several of the constituents found in the solid phase of the sediment. A concentration gradient from the surface to buried sediment occurs for the total concentration of arsenic, copper, lead, silver, zinc, and sulfur (fig. E-3). A series of sequential extractions provided additional details of the distribution of arsenic, copper, and zinc. Each constituent was extracted first with a reagent that attacked amorphous iron and manganese oxyhydroxides, then with a reagent that attacked organically bound material, and finally, with a reagent that attacked the residual sulfides (Chester and Hughes, 1967; Chao and Sanzolone, 1977). The results, shown in figure E-4, suggest that arsenic, copper, and zinc are precipitated as sulfides.

The trend displayed by solid phase arsenic suggests that an analytical method to distinguish between As(III) and As(V) in solid phase material would provide more insight into the mechanism of deposition of arsenic. We have developed such a method. We used the method to determine the concentration of available arsenic in another series of samples collected at the location in the reservoir where the greatest concentration of arsenic occurred in the interstitial water (8,900 micrograms per liter). The samples were collected at 25-cm intervals of a hole after augering to the appropriate depth; each sample was placed in a plastic bag, stored on ice, and finally, frozen within an hour. The samples were collected for each interval to 275 cm, at which point the hole began to cave in. Some more material was collected at about 300 to 350 cm. We extracted the arsenic from the wet, thawed sample with 4.0 normal hydrocholoric acid (HCl). Recovery of spikes of As(III) and As(V) added to the samples indicate that no oxidation or reduction of extracted arsenic occurs during the short interval required to extract the arsenic and begin separation of the two oxidation states.

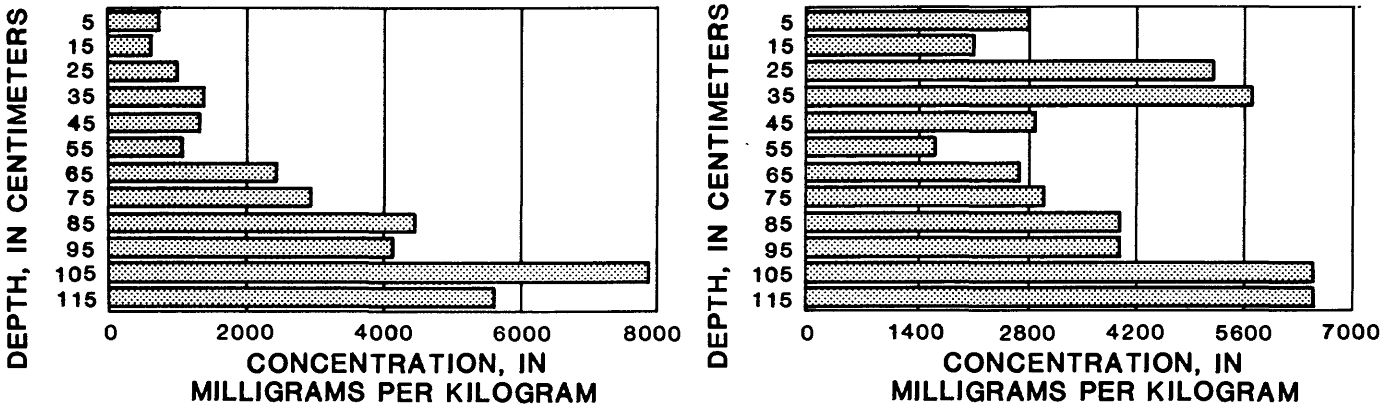
[1] U.S. Geological Survey, Denver, Colo.

[2] University of Montana, Department of Geology, Missoula, Mont.



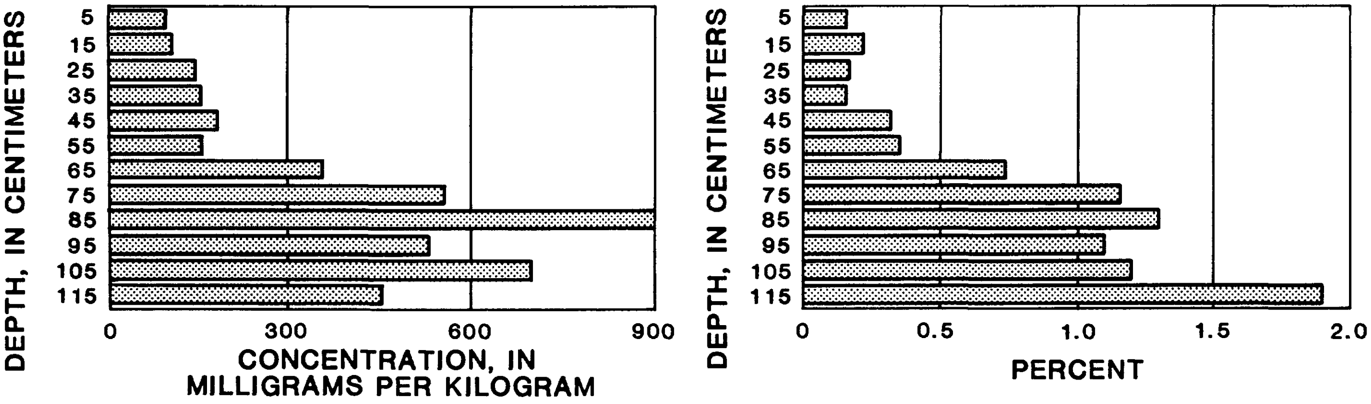
TOTAL ARSENIC IN CORE 5

TOTAL SILVER IN CORE 5



TOTAL COPPER IN CORE 5

TOTAL ZINC IN CORE 5



TOTAL LEAD IN CORE 5

TOTAL SULFUR IN CORE 5

Figure E-3.—The concentration gradient for arsenic, copper, lead, silver, zinc, and sulfur.

Results for the extraction of available arsenic from the augered samples are illustrated in figure E-5. Arsenic occurred primarily as As(V) in the first 75 cm; all of the arsenic was extracted. Below 75 cm some As(III) occurred along with the As(V), however, the sum of the concentrations of As(III) and As(V) does not equal the total concentration of arsenic that was determined independently by hydrofluoric, perchloric, and nitric acid digestion. The remainder of the arsenic was extracted from the residue of the 4.0 normal HCl extraction by the procedure of Chao and Sanzolone (1977). The sum of the concentrations of As(III), As(V), and the concentration of As determined in the sulfide extraction closely approximates the total arsenic concentration.

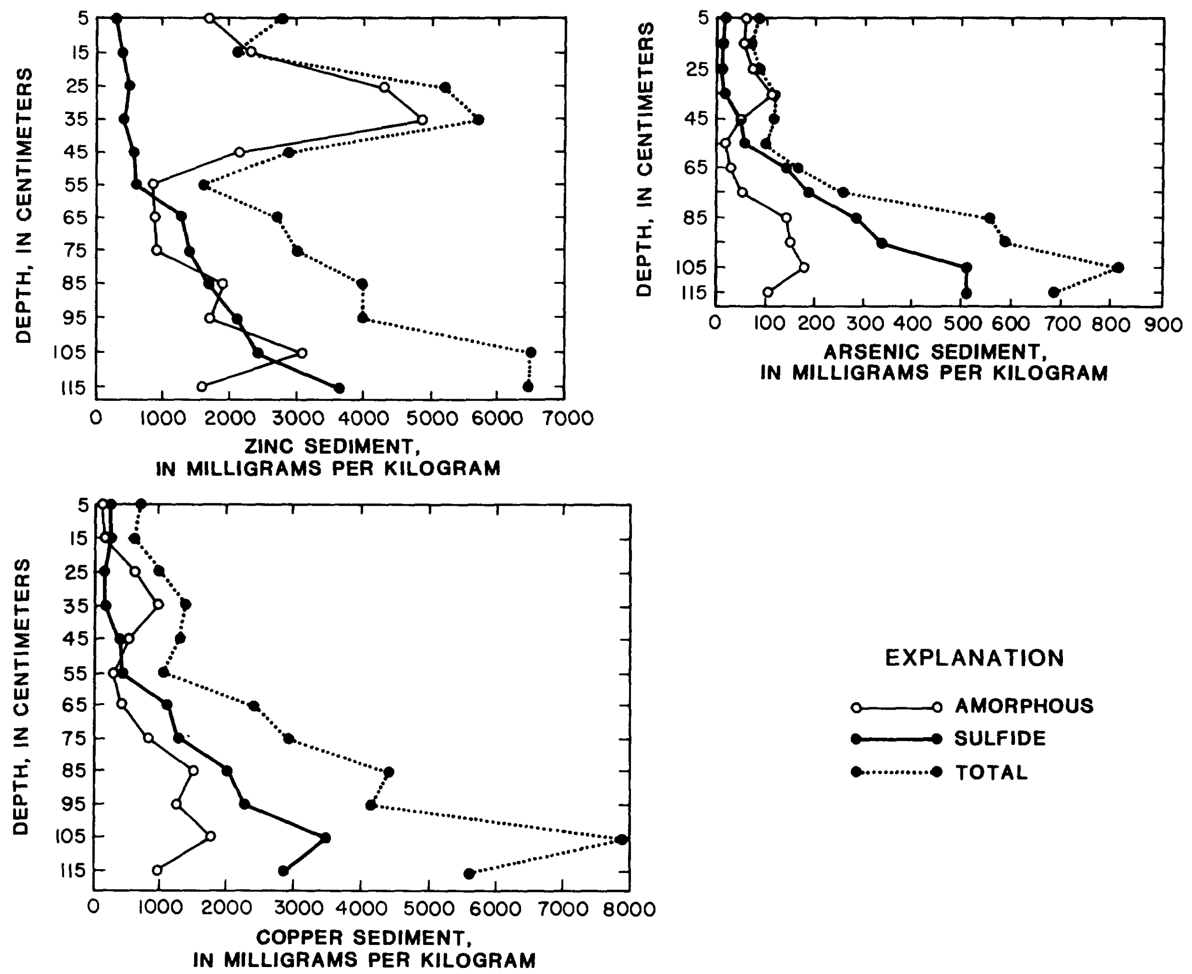


Figure E-4.—The abundance of constituents associated with amorphous material and associated with sulfides.

We conclude from the data presented in figure E-5 that the arsenic entered the reservoir in the solid state adsorbed on iron and manganese hydroxides. The arsenic has remained in this condition in the first 75 cm of the sediment. When the sediments were buried reduction occurred, releasing ferric iron and As(V). These constituents in turn are reduced to ferrous iron and As(III). The reduction of sulfate produced hydrogen sulfide, which precipitated some of the As(III) as arsenious sulfide or arsenopyrite. However, when all of the sulfate had been reduced there was insufficient sulfide to precipitate arsenic, resulting in soluble arsenic in the interstitial water, thus the contamination of the ground water with arsenic.

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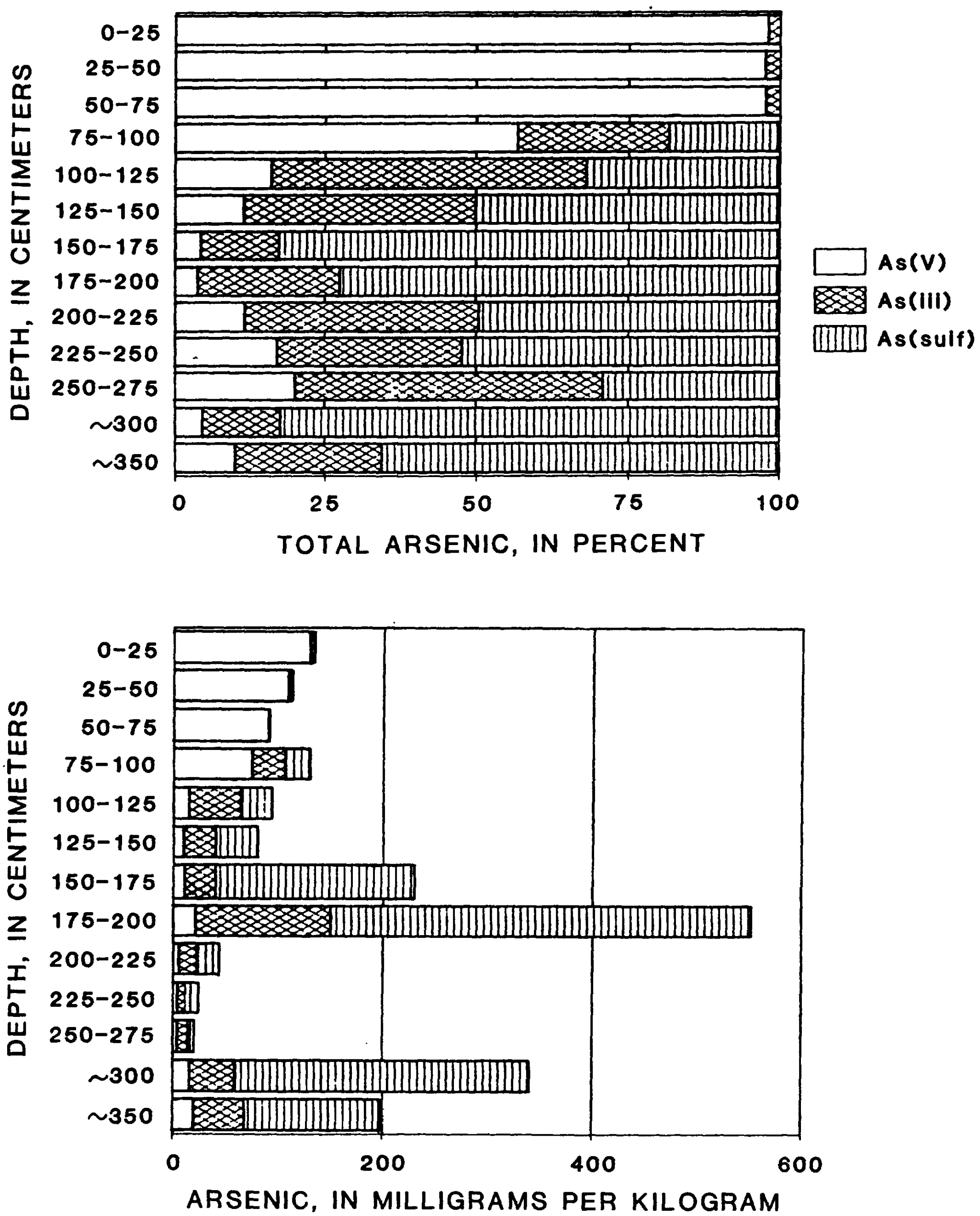

Figure E-5.—The concentration of As(V) and As(III) determined from the 4.0 normal hydrochloric acid extraction of sediment of Milltown Reservoir and residual arsenic determined from the sulfide extraction.

RECONNAISSANCE APPRAISALS OF ANTHROPOGENIC EFFECTS ON REGIONAL GROUND-WATER QUALITY

By Doug Cain[1], Dennis R. Helsel[2], and Stephen E. Ragone[2]

INTRODUCTION

During 1984, the U.S. Geological Survey began regional ground-water-quality appraisals in 14 areas nationwide as part of its Toxic Waste—Ground-Water Contamination Program. These appraisals are intended to develop and test procedures to provide information about regional ground-water chemistry with emphasis on trace elements and organic constituents and to explain ground-water quality in terms of effects of local hydrology and anthropogenic (human) activities for a wide variety of hydrologic and human environments. Towards this goal, the studies were designed in five phases to evaluate the hypothesis that human activities, defined by a variety of land uses, have a predictable effect on ground-water quality (Helsel and Ragone, 1984). The five-phase approach includes: (1) reconnaissance, (2) experimental design, (3) data collection, (4) data analysis, and (5) verification of conclusions in a similar area.

During the reconnaissance phase, existing hydrogeologic, land-use, and water-quality data were compiled and evaluated, and, in some studies new data were collected. As a result, a conceptual model of the predominant factors affecting ground-water quality was developed for each study area. The ground-water system of each area was characterized to define areas of recharge and discharge, and to provide an estimate of ground-water residence time. Ground water less than 100 years old was considered susceptible to contamination by human activity and was the focus of these studies. Because of the regional nature of the studies, use of water-quality data from wells contaminated by point sources was avoided.

The quantity and quality of available land-use information varied considerably between study areas. In one area, ground-water quality associated with 10 distinct land uses could be evaluated; however, in other areas, land-use information had to be generalized into 2 to 4 broader categories. Because land uses usually do not occur homogeneously over large areas, several of the studies devised methods to assign one land use to a given well, where more than one land use may have existed near the well.

The availability of water-quality data, especially for organic constituents, ranged from minimal or no data in several study areas to several hundred analyses in one study area. If sufficient data were available, statistical techniques were used to evaluate differences in ground-water quality associated with different land uses. Because of the diversity in hydrogeologic setting and in the availability of land-use and water-quality data, results of the reconnaissance studies indicated considerable variation in conclusions about anthropogenic effects on regional ground-water quality. Results of the reconnaissance appraisals made in eight of the study areas (table E-2) are summarized in this abstract. The other six study areas had insufficient data to reach conclusions about anthropogenic effects on regional ground-water quality.

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

[2] U.S. Geological Survey, Reston, Va.

Table E–2.—*Location, hydrogeologic setting, and mean annual precipitation of eight regional study areas for appraisal of regional ground-water quality*

Location	Hydrogeologic unit	Mean annual precipitation (centimeters)
Long Island, New York	Upper glacial aquifer	112
New Jersey	Potomac-Raritan-Magothy aquifer system	112
Connecticut	Stratified drift aquifers	109–119
Central Florida	Upper Floridan aquifer and overlying aquifers	135
Nebraska	High Plains aquifer	30–99
Colorado	Fountain Creek alluvial aquifer	28–41
Texas	Edwards aquifer	53–86
New Mexico	Albuquerque-Belen basin alluvial aquifer	23

LONG ISLAND, NEW YORK

Contamination from human activities, as measured by differences in concentrations of water-quality constituents in samples collected from 903 wells representing 10 land-use categories, has affected waters of the upper glacial aquifer on Long Island (Eckhardt and others, in press). Largest concentrations of nitrate, chloride, and dissolved solids were in samples collected from wells in agricultural, commercial, and high-density residential areas; smallest concentrations of these constituents were in samples collected from wells in undeveloped, recreational, and low- and medium-density residential areas.

The most commonly detected purgeable organic compounds were 1,1,1-trichloroethane (24 percent of wells sampled); tetrachloroethylene (20 percent of wells sampled); trichloroethylene (18 percent of wells sampled); chloroform (9 percent of wells sampled); and 1,2-dichloroethylene (5 percent of wells sampled). Trichloroethylene, 1,1,1-trichloroethane, and tetrachloroethylene were detected most frequently (more than 40 percent of wells sampled) in ground water from commercial and industrial areas, and detection frequencies were only slightly smaller (20–40 percent) in medium- and high-density residential land-use areas. The same compounds were detected less frequently in samples collected from wells in institutional, recreational, and transportation areas; these compounds were not detected, or they were detected infrequently in ground water from undeveloped, agricultural, and low-density residential areas. Chloroform was the only purgeable organic compound detected in water from all 10 land-use categories. The percentage of wells that showed detectable concentrations of trichloroethylene and 1,1,1-trichloroethane was correlated directly with population density near the wells. The coefficients of determintation (R^2) of a linear regression between percentage of detections and population density were 0.69 for trichloroethylene and 0.72 for 1,1,1-trichloroethane.

NEW JERSEY

Differences in the concentrations of selected water-quality constituents among undeveloped, agricultural, and urban land-use areas were evaluated using data from 71 wells located in or near the outcrop area of the Potomac-Raritan-Magothy aquifer system of northern New Jersey (Barton and others, in press). Water from wells associated with undeveloped land had the smallest pH and the smallest concentrations of dissolved oxygen and nitrate, the largest concentrations of most trace elements, and the most frequent detection of phenols. These characteristics indicate that the effects of wetlands, which make up about two-thirds of the undeveloped land, dominate ground-water quality in the aquifer underlying undeveloped lands in the area. Naturally occurring dissolved organic carbon in the wetlands environment can decompose and release phenols, and decrease dissolved-oxygen concentrations. Small dissolved-oxygen concentrations in combination with small values of pH can produce increased concentrations of trace elements. Water samples collected from wells in agricultural areas had the smallest concentrations of major ions and most trace elements, the largest concentrations of dissolved oxygen and copper, and the most frequent detection of pesticides (18 percent of wells sampled). Water samples collected from wells in urban areas had the largest concentrations of nitrate, and the most frequent detection of purgeable organic compounds (29 percent). The frequency of detection of purgeable organic compounds in the three land-use categories in the study area was similar to frequencies of detection found in samples from 179 wells in the same land-use categories in the outcrop area of the Potomac-Raritan-Magothy aquifer system southwest of the study area (Fusillo and others, 1984).

CONNECTICUT

Activities associated with agricultural, residential, and industrial-commercial land uses have affected the quality of ground water in two small, stratified-drift aquifers in Connecticut compared to the quality of ground water in undeveloped areas of the same two aquifers (Grady and Weaver, in press). These comparisons are based on data from 38 previously existing wells and 21 newly installed wells in the aquifers; these aquifers underlie 20.5 and 32.9 km^2 (square kilometers). Median concentrations of most constituents analyzed were smallest in undeveloped areas. Ground water in agricultural areas had the largest median sulfate and total ammonia plus organic nitrogen concentrations. Ground water in residential areas had significantly larger median specific conductance, hardness, calcium, magnesium, chloride, and dissolved solids concentrations than ground water in undeveloped areas. Ground water in industrial-commercial areas had the largest median values of specific conductance and pH, and the largest concentrations of calcium, magnesium, chloride, bicarbonate, dissolved solids, boron, and strontium. Arsenic, beryllium, lead, and lithium were detected more frequently in ground water from industrial-commercial areas than in areas with the other three land uses. No significant water-quality differences were found between the same land uses in the two aquifers, indicating that the conclusions may be transferable to other stratified-drift aquifers. The only sample that had detectable concentrations of purgeable organic compounds was from an industrial-commercial land-use area.

CENTRAL FLORIDA

The effects from man's activities on ground-water quality in three areas in central Florida were evaluated and compared to ground-water quality in one control area (Rutledge, in press). The three study areas were: (1) an urban area where stormwater is disposed of in drainage wells open to the Upper Floridan aquifer; (2) a citrus grove area where pesticides and fertilizers are used extensively and could contaminate the surficial aquifer overlying the Upper Floridan aquifer; and (3) an area where phosphate ore is mined and processed, and potential exists to contaminate the surficial aquifer, an intermediate aquifer, and the Upper Floridan aquifer. The control area consisted primarily of forest with some rangeland, wetlands, and open water. The appraisal included analysis of surface water and sediment near probable sources of contamination, and 33 ground-water samples collected in the 4 areas.

Purgeable organic compounds were the most common contaminants in the Upper Floridan aquifer within the urban area. Pesticides, including simazine and diazinon, found in water from the surficial aquifer, were the most common contaminants in the citrus grove area. Zinc and copper, which are associated with pesticides and fertilizers, were found in larger concentrations in samples collected from wells in the surficial aquifer underlying the citrus grove area than in samples collected from wells in the same aquifer underlying the control area. Concentrations of arsenic, selenium, mercury, manganese, and iron were larger in ground water underlying the phosphate-mining area than in ground water underlying the control area.

NEBRASKA

Agriculture is the primary land use in Nebraska, comprising over 90 percent of the land use in the State. Because this single land use is so predominant in the area overlying the High Plains aquifer, a comparison of water quality associated with other land uses was not appropriate. Instead, the study in Nebraska focused on the relations between concentrations of nitrate and triazine herbicides in ground water and: (1) selected hydrogeologic variables, (2) irrigation-well density, and (3) other agriculture-related variables (Chen and Druliner, in press). The results are based on nitrate analyses of samples collected from 81 wells and triazine herbicide analyses of samples collected from 57 wells in 6 areas of Nebraska.

Concentrations of nitrate were larger in irrigated areas with two or more irrigation wells per 2.59 km^2 than in irrigated areas with fewer than two wells. Triazine herbicides were detected more frequently in areas with two or more irrigation wells per 2.59 km^2 than in irrigated areas with fewer than two wells. Concentrations of nitrate had significant ($\alpha<0.05$) positive correlations with irrigation well density, hydraulic conductivity, annual precipitation, and specific discharge; concentrations of nitrate had significant negative correlations with well depth, depth to water, and hydraulic gradient. Concentrations of triazine herbicide had significant positive correlations with irrigation-well density, hydraulic conductivity, annual precipitation, specific discharge, and nitrate concentration.

COLORADO

The reconnaissance appraisal in Colorado evaluated anthropogenic effects on ground-water quality in the alluvial aquifer along Fountain Creek, a stream that receives a large volume of sewage effluent from the city of Colorado Springs, Colo. The aquifer is pumped extensively for municipal use in the primarily urban upgradient one-third of the study area, and for agricultural use in the downgradient two-thirds of the study area. Results of this appraisal are based on existing analyses of water-quality samples collected from 103 wells, new analyses of samples collected from 20 existing wells, and existing and newly collected water-quality data for Fountain Creek.

Major ions, boron, lithium, strontium, and uranium increased in concentration downgradient and had significantly larger concentrations in the agricultural land-use area (Cain and Edelmann, in press). However, the increases resulted from: (1) evaporative concentration caused by water use and reuse, (2) dissolution of minerals in the aquifer and underlying shale bedrock, and (3) tributary ground-water inflows, rather than as a direct result of the agricultural land use. Concentrations of nitrite plus nitrate and detergents were larger in the predominantly urban, upgradient part of the alluvial aquifer because of pumpage-induced recharge of water from Fountain Creek; the larger concentrations are not related directly to urban land use. Purgeable organic compounds were detected in 55 percent of the 20 wells sampled. The most frequently detected purgeable organics were chloroform and 1,1,1-trichloroethane. Insufficient data were available to evaluate statistically the differences in the occurrence of purgeable organic compounds between the agricultural and urban land-use areas.

TEXAS

Differences in ground-water quality in the Edwards aquifer were evaluated using data from 280 wells and 3 springs distributed over 5 land-use categories and 4 aquifer subareas (P. M. Buszka, U.S. Geological Survey, written commun., 1986). The aquifer subareas were classified to indicate susceptibility to ground-water contamination, based on ground-water flow patterns, tritium concentrations in ground water, and geologic information. Aquifer subarea 1 includes the outcrop area and areas with tritium concentrations greater than 20 tritium units, indicating recharge during the last 30 years. Aquifer subarea 2 includes a mixing area between the unconfined and confined zones of the aquifer; aquifer subarea 2 may receive some recharge from land surface. Aquifer subareas 3 and 4 are confined in most areas, and receive little or no direct recharge from land surface.

Samples from land use classified as cropland had the largest concentrations of nitrite plus nitrate in aquifer subarea 1. Larger concentrations of nitrite plus nitrate were associated with larger concentrations of tritium. Nitrogen-isotope ratios indicate that recharge from streamflow may account for nearly all nitrate in the Edwards aquifer. Most of the occurrences of tetrachloroethylene, 1,2-(trans)-dichloroethylene, trichlorofluoromethane, 1,1,1-trichloroethane, and 2,4-D in ground water were associated with urban land use in aquifer subareas 1 and 2.

NEW MEXICO

The reconnaissance appraisal of the Albuquerque-Belen basin alluvial aquifer primarily used existing data to delineate susceptible areas of ground-water contamination on the basis of hydrogeologic and land-use factors. Ground water in most of the Albuquerque-Belen alluvial basin is relatively less susceptible to contamination from the land surface because: (1) depth to water is larger than 30 m (meters); (2) open space, including rangeland and Indian reservations, is the predominant land use; and (3) the small quantity of annual precipitation (table E–2) results in no natural mechanism for recharge to the ground-water system exists (Anderholm, in press). However, part of the basin includes the Rio Grande Valley where depth to water generally is smaller than 10 m, and recharge to the ground-water system results from infiltration from the Rio Grande and from applied irrigation water. Much of the urban land use in the basin is in this area. This combination of factors causes relatively greater susceptibility to contamination. Ground-water contamination has been documented in several areas of the Rio Grande Valley near Albuquerque, N.M. Both organic and inorganic contaminants have been identified. Organic contaminants included purgeables, aliphatic hydrocarbons, and polycyclic compounds; inorganic contaminants included iron and arsenic.

CONCLUSIONS

The reconnaissance appraisals of the anthropogenic effects on regional ground-water quality summarized in this abstract resulted in preliminary conclusions relating land use to ground-water quality. These conclusions primarily resulted from evaluation of existing data and are subject to the difficulties inherent in such evaluations. The conclusions are the basis for continuing studies in the first six study areas listed in table E–2. Experimental design, the next phase in the study approaches, is nearing completion; it will form the basis for additional data collection and analysis to test statistically the preliminary hypotheses about anthropogenic effects on regional ground-water quality that were developed during the reconnaissance phase of the study.

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